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16. Abstract Poly (vinylene carbonate) which was polymerized from the purified monomer as required was evaluated in the form of thin or ultrathin films to demonstrate the high flux potential of this polymer. To conserve the limited supply of polymer and to determine the effect of polymer molecular weight on the osmotic properties of the films, thin, knife-cast films were prepared from dilute solutions of the polymers and evaluated. Knife-cast films of 1.2$_u$ thickness on greater gave high salt retentions (85.2 to 98.2%) over 5.0 to 20.5 hours operation with 35,000 ppm feed solution at 1500 psi. Films of 0.71 to 0.76$_u$ thickness also exhibited high initial salt retentions (92.7 to 98% retention with 2.0 to 4.5 gfd flux) but showed increasing flux and decreasing salt retention with time and eventual loss of useful osmotic properties. Copolymers of vinylene carbonate were prepared and evaluated in an effort to obtain an internally plasticized membrane or film suitable for long-term reverse-osmosis service at 1500 psi. The vinylene carbonate/vinyl acetate copolymers in mole ratios of 5/1, 3.3/1 and 1.6/1 were prepared and evaluated. The tensile properties of the vinylene carbonate/vinyl acetate copolymers showed, however, that the desired plasticizing properties were not obtained. Attempts to prepare a copolymer from vinylene carbonate and N-vinyl-2-pyrrolidone comonomers in bulk by initiation with AIBN catalyst at 65°C were not successful, in spite of successively more stringent purifications of the vinylpyrrolidone. The investigation of other new polymers

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Abstractor Lee M. Kindley | Institution Office of Saline Water

included the evaluation of dense films of poly (diacetone acrylamide). A low salt permeability (D_2K = 2.58 x 10^{-12} cm ^{2}/sec) was exhibited by this material, but it was concluded that the low product water flux obtained during reverse-osmosis testing was caused by extrusion of the film into the support because of its poor mechanical properties. Acetone soluble nitrile polymers and copolymers prepared from methacrylonitrile were investigated in an effort to utilize the highly polar nitrile group along with the outstanding strength and stability of these polymers. Acid hydrolysis of polymethacrylonitrile resulted in a modified polymer containing up to 9.5% carboxyl groups. Films of the hydrolyzed polymer gave calculated fluxes of 2.0 to 14.9 gfd (based on a 2500 A thickness) with salt retentions of 23 to 38%. Films of a microcrystalline form of collagen were also evaluated for reverse-osmosis properties. Polymer blends of ethyl cellulose, 48.5% ethoxyl content, and poly (diacetone acrylamide) (PDAA) were investigated in an effort to obtain a film with a salt retention approaching that of ethyl cellulose but with increased water flux. The incorporation of 10% PDAA into ethyl cellulose resulted in films with salt retentions of 98.3 to 99.5%.

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Research and Development of New Polymer Systems for Reverse Osmosis Membranes

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UNITED STATES DEPARTMENT OF THE INTERIOR • Stewart L. Udall, Secretary
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FOREWORD

This is one of a continuing series of reports designed to present accounts of progress in saline water conversion and the economics of its application. Such data are expected to contribute to the long-range development of economical processes applicable to low-cost demineralization of sea and other saline water.

Except for minor editing, the data herein are as contained in a report submitted by the contractor. The data and conclusions given in the report are essentially those of the contractor and are not necessarily endorsed by the Department of the Interior.

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INTRODUCTION AND SUMMARY

This program was undertaken with the objective of the development of new polymers that would yield reverse-osmosis membranes superior to cellulose acetate membranes in osmotic and mechanical properties and in chemical stability.

Cellulose acetate membranes have demonstrated promising performance for the reverse-osmosis desalination of brackish waters at approximately 800 psi pressure. They are subject, however, to chemical and biological degradation and care must be taken to avoid conditions which favor these forms of attack. The useful life of cellulose acetate membranes is also affected by a pressure dependent flux decline. This is especially pronounced at the high applied pressures (e.g., 1500 psi) required for seawater desalination. It is believed that the flux decline of cellulose acetate membranes is related to plastic deformation under the operating pressures encountered during reverse-osmosis operation. The susceptibility of cellulose acetate to hydrolytic and biological attack is related to the structural features of the polymer; cleavage of both in-chain oxygen linkages and the pendent acetate groups can occur. Cleavage of the in-chain acetal linkage is effected by certain biological agencies and leads to a reduced molecular weight of the polymer with a decline in the mechanical properties of the membrane. Hydrolysis of the acetate groups by either chemical or biological means adversely affects the osmotic properties of the membrane. The achievement of maximum durability in the polymer, therefore, would be obtained with polymers which have good osmotic and mechanical properties and are resistant to chemical and biological attack.

One of the most stringent requirements of an asymmetric membrane is its resistance to the compressive stresses during reverse osmosis operation. Excessive compression of the spongelike supporting layer tends to reduce product water flux and may damage the thin, active, desalinating layer. Thus, a high compressive yield point is necessary to prevent plastic deformation which can result in permanent damage to the membrane. High compressive strengths are found in polymers which are crystalline or at least possess a high degree of interchain association. Crystallinity, however, must be controlled to prevent extreme brittleness and allow a certain amount of plastic flow to accommodate the irregularities present in support plates without membrane rupture. The polar groups most effective in increasing interchain association and polymer stiffness are the proton-donor groups such as hydroxyl,

amino and carboxyl which can hydrogen-bond with each other. Ester, carbonyl and nitrile groups also tend to associate and impart improved strength to the polymer.

In addition to structural stability, membrane polymers must be capable of the sorption of up to 20% by weight of water in order to provide rapid water transport while rejecting the passage of salt ions. The polar groups which provide structural stability also tend to provide the capability for water sorption through the formation of hydrogen bonds.

For the greatest chemical stability, polymer types with the most stable linkages in the main chain and pendent groups are necessary. In-chain linkages not easily susceptible to hydrolytic attack and small polar pendent groups such as hydroxyl, nitrile and amide groups which are resistant to chemical attack, will provide the best chemical stability.

It is difficult, of course, to find all of the properties suggested above in one polymer. The polymers which were chosen for investigation in this program, however, were those thought to best combine the properties believed most important to osmotic performance and improved durability.

Previous work had demonstrated that poly(vinylene carbonate) films have a theoretical salt rejection of 98.9% with a water permeability from 2.0 to 2.5 times as great as that of cellulose acetate, indicating the potential for very high flux membranes from this polymer. Solvents for poly(vinylene carbonate) which dissolve more than 5.5% of the polymer are limited to high-boiling types which are not well suited to the preparation of asymmetric membranes. Consequently, attempts to make asymmetric membranes from poly(vinylene carbonate) with fluxes similar to those from cellulose acetate membranes did not meet with success. Although chemical modification of poly(vinylene carbonate) provided solubility in more suitable solvents, the acetone-soluble modification (polyacetoxymethylene) was of insufficient mechanical strength. Work with poly(vinylene carbonate) in the present program, therefore, was limited to the demonstration of high flux from thin or ultrathin films. Copolymers of vinylene carbonate and vinyl acetate were prepared and evaluated in an effort to internally plasticize the polymer when tests revealed the vinylene carbonate homopolymer was excessively brittle. External plasticizers for poly(vinylene carbonate) including poly(diacetone acrylamide) and a polyurethane were also evaluated in attempts to reduce the brittleness of the polymer.

Further studies were also conducted in an effort to adapt the highly durable nitrile polymers for membrane use. Previous studies indicated that polyacrylonitrile was difficult to form into an asymmetric membrane because of the high-boiling solvents required and in addition its water sorption capability appears to be insufficient for high flux with high salt retention. Therefore, the acetone-soluble polymethacrylonitrile was evaluated along with its

partially hydrolyzed derivatives and its copolymers with acrylamide or with vinylpyrrolidone in an effort to provide a nitrile polymer with desirable solubility and water sorption properties.

New polymers or new forms of polymers recently developed were also evaluated as new membrane materials. These included poly(diacetone acrylamide) prepared from the newly available monomer and a microcrystalline form of collagen which was interesting because of its highly crystalline nature and its high content of chemically bound water.

Melamine formaldehyde films were prepared and evaluated in attempts to explain the improved salt retentions obtained in pilot plant runs in which the feed contained melamine formaldehyde resin leached from a filter element.

It has been recognized for some time that ethyl cellulose has excellent salt rejection capabilities and that it can be made into films with good strength and flexibility. Because of its resistance to alkaline hydrolysis, it should be a candidate for very durable membranes, but its lack of high water permeability and its failure as an ultrathin membrane have made it a laboratory curiosity. Therefore, an investigation was conducted into the preparation of ethyl cellulose membranes with increased water flux over that of previously reported work by using material of the lowest ethoxyl content commercially available. The status of development of membranes from all the new polymer types investigated is summarized below.

Poly(vinylene carbonate) which was polymerized from the purified monomer as required was evaluated in the form of thin or ultrathin films to demonstrate the high flux potential of this polymer. To conserve the limited supply of polymer and to determine the effect of polymer molecular weight on the osmotic properties of the films, thin, knife-cast films were prepared from dilute solutions of the polymers and evaluated. Knife-cast films of 1.2 μ thickness or greater gave high salt retentions (85.2 to 98.2%) over 5.0 to 20.5 hours operation with 35,000 ppm feed solution at 1500 psi. Films of 0.71 to 0.76 μ thickness also exhibited high initial salt retentions (92.7 to 98% retention with 2.0 to 4.5 gfd flux) but showed increasing flux and decreasing salt retention with time and eventual loss of useful osmotic properties. Increasing the molecular weight of the poly(vinylene carbonate) from 160,000 to 800,000 resulted only in a retardation in the extent of breakdown of the film with little increase in useful life. Heat-treating the poly(vinylene carbonate) film to 86°C also failed to prevent eventual breakdown of the film during 4 to 20 hours of testing.

Thinner, more perfect polymer films were prepared by the Carnell method. Ultrathin films of cellulose acetate (750 to 11,000 Å thickness) were prepared first to develop the necessary technique of this method. The cellulose acetate ultrathin films exhibited acceptable stability of osmotic properties during the 20 to 72 hour testing period at 1500 psi with 3.5% sodium chloride feed solution.

Ultrathin films prepared by the Carnell method from poly(vinylene carbonate) of 160,000 molecular weight in the thickness range from 3740 to 6000 Å exhibited an increase in flux and a decrease in salt retention with time (1.0 to 10.5 hours testing). Increasing the molecular weight of the polymer to 400,000 resulted in ultrathin films which were somewhat more durable but eventually showed increasing flux after 4.5 hours operation. The ultrathin films of poly(vinylene carbonate) thus paralleled the results found with the thin, knife-cast films.

The loss of osmotic properties of poly(vinylene carbonate) films in extended-time testing suggested a mechanical breakdown of the film and therefore the tensile properties of poly(vinylene carbonate) were determined and compared with cellulose acetate. This comparison revealed that although poly(vinylene carbonate) has a higher tensile strength, it is much more brittle than cellulose acetate, which is more ductile, undergoes plastic deformation more readily and is tougher than the former. The brittle nature of poly(vinylene carbonate) offered a plausible explanation for the failure of thin and ultrathin films under reverse osmosis test conditions and indicated that chemical modification of the polymer to reduce brittleness was required.

Copolymers of vinylene carbonate were prepared and evaluated in an effort to obtain an internally plasticized membrane or film suitable for long-term reverse-osmosis service at 1500 psi. The vinylene carbonate/vinyl acetate copolymers in mole ratios of 5/1, 3.3/1 and 1.6/1 were prepared and evaluated. The tensile properties of the vinylene carbonate/vinyl acetate copolymers showed, however, that the desired plasticizing properties were not obtained. Instead, an increased brittleness was noted in the 5/1 and 3.3/1 copolymers. With the greater vinyl acetate content of the 1.6/1 copolymer a yield point appeared, indicating incipient plasticization, but the elongation was still far too low for adequate flexibility. The incorporation of vinyl acetate [at least in amounts less than 38.5 mole% (1.6/1)] apparently increased the intermolecular forces of attraction within the copolymer, resulting in an anti-plasticizing or embrittling effect.

Both salt retention and flux decreased as more vinyl acetate was incorporated into the vinylene carbonate/vinyl acetate copolymer (up to 38.5 mole% vinyl acetate). The decrease in salt retention appears to be linear with the number of acetate groups substituted for vinylene carbonate groups. The flux decrease was much greater than a linear decline, however, and reached a value in the 1.6/1 copolymer approximately one-tenth that of the vinylene carbonate homopolymer. The vinyl acetate apparently interferes with water transport through the membrane.

Attempts to prepare a copolymer from vinylene carbonate and N-vinyl-2-pyrrolidone comonomers in bulk by initiation with AIBN catalyst at 65°C were not successful, in spite of successively more stringent purifications of the vinylpyrrolidone. The polyvinylpyrrolidone or poly(vinylene carbonate)

homopolymers could be prepared under the same conditions. Apparently, the impurities still present in N-vinyl-2-pyrrolidone did not prevent homopolymerization but did prevent copolymerization with vinylene carbonate.

The investigation of other new polymers included the evaluation of dense films of poly(diacetone acrylamide). A low salt permeability (D_2K = 2.58 x 10^{-12} cm^2/sec) was exhibited by this material, but it was concluded that the low product water flux obtained during reverse-osmosis testing was caused by extrusion of the film into the support because of its poor mechanical properties. Because poly(diacetone acrylamide) was highly plasticized by water, it was also investigated as an external plasticizer for poly(vinylene carbonate). Tensile property data showed that 7.7% of added poly(diacetone acrylamide) acted as a very weak plasticizer but it did not improve the reverse-osmosis properties of poly(vinylene carbonate) in blends up to 14.7%. Polyacetoxymethylene was prepared as an acetone soluble derivative of poly(vinylene carbonate). Dense films of this material were excessively brittle and weak and not suitable for testing. Melamine-formaldehyde films contained imperfections and could not be tested for reverse-osmosis properties.

Acetone soluble nitrile polymers and copolymers prepared from methacrylonitrile were investigated in an effort to utilize the highly polar nitrile group along with the outstanding strength and stability of these polymers. Acid hydrolysis of polymethacrylonitrile resulted in a modified polymer containing up to 9.5% carboxyl groups. Films of the hydrolyzed polymer gave calculated fluxes of 2.0 to 14.9 gfd (based on a 2500 Å thickness) with salt retentions of 23 to 38%. The increased salt retention over that of the unmodified polymethacrylonitrile was not enough to warrant further work. Aqueous emulsion copolymerizations resulted in the incorporation of only 4% vinylpyrrolidone into the methacrylonitrile-vinylpyrrolidone copolymer and only 1% acrylamide into the methacrylonitrile-acrylamide copolymer. Apparently homopolymerization predominated over copolymerization and resulted in the low incorporation of the corresponding comonomers. The salt retention of these copolymers showed little improvement over that for the homopolymer, polymethacrylonitrile, and work was discontinued.

Films of a microcrystalline form of collagen were evaluated for reverse-osmosis properties. Collagen films were prepared by casting from colloidal collagen dispersions (0.25 to 1.0%) in organic solvent-water mixtures. Collagen films of 0.65 mils dry and 3.2 mils wet thicknesses which were not heat-treated had fluxes of 4.1 to 4.7 gfd (corresponding to as high as 1540 gfd for a 2500 Å thickness) and salt rejections of 23 to 25.1%. Heat-treatment of the collagen film at 150°C gave reduced fluxes (up to 657 gfd calculated for a 2500 Å thickness) and increased desalination (28.2 to 33.9% salt rejection). Heat-treatment of a collagen film (0.48 mil thickness) containing hexamethoxymethylmelamine crosslinking agent (8% based on collagen) at 150°C gave the lowest flux corresponding to 56.4 gfd for a 2500 Å thickness and the highest salt retention (43.2 to 47.2%). Supported collagen films were also prepared by casting the dispersions on Metricel filters.

Because of the high water transport properties, microcrystalline collagen films were evaluated with respect to brackish water desalination using 1.0% magnesium sulfate solution at 800 psi. Collagen films crosslinked by heat alone gave 69.3 to 74.8% magnesium sulfate retention and product water fluxes of 5.1 to 5.8 gfd (calculated fluxes of 228 to 769 gfd for a 2500 Å thickness).

Polymer blends of ethyl cellulose, 48.5% ethoxyl content, and poly(diacetone acrylamide) (PDAA) were investigated in an effort to obtain a film with a salt retention approaching that of ethyl cellulose but with increased water flux. The incorporation of 10% PDAA into ethyl cellulose resulted in films with salt retentions of 98.3 to 99.5%. The calculated D_1C_1 from the measured reverse-osmosis data (5.27×10^{-9} g/cm-sec) on the films from the blend corresponded to about the same D_1C_1 reported from osmosis data (3.9×10^{-9} g/cm-sec) for pure ethyl cellulose films. This data showed that the added PDAA at the 10% level did not increase the flux of films derived from blends over those made from pure ethyl cellulose.

Efforts were directed towards increasing the flux of ethyl cellulose by using a lower ethoxyl content material. Ethyl cellulose of 44.7% ethoxyl content has a moisture absorption ~ 60% greater than the 48.5% ethyl cellulose used for blending with poly(diacetone acrylamide). The ethyl cellulose with 44.7% ethoxyl content was therefore evaluated in the form of asymmetric membranes for reverse-osmosis characteristics. The optimum formulation and casting conditions were not achieved but a salt rejection of 93.3% at a flux of 4.25 gfd was obtained when tested with 3.5% sodium chloride solution at 1500 psi.

POLY(VINYLENE CARBONATE)

Poly(vinylene carbonate) was shown to have excellent intrinsic osmotic properties in previous work;[1] however, efforts to realize the predicted high fluxes and salt retentions in asymmetric membranes[2] did not meet with success. Therefore, the emphasis on this program was shifted toward the evaluation of thin or ultrathin films to demonstrate high fluxes under reverse-osmosis conditions.

THIN, KNIFE-CAST FILMS

Knife-cast films of poly(vinylene carbonate) between 0.7 and 7.0 microns (μ) in thickness were evaluated primarily to conserve the supply of polymer. Sufficient film for three 3-in.-dia test circles required only a few milliliters of casting solution which could be made up quickly from small supplies of polymer. This method was used, therefore, to evaluate the effect of polymer molecular weight on film properties and durability before switching to ultrathin films which often exhibit fewer flaws but require much larger polymer samples (~ 1 liter of solution) for their preparation.

A Gardner adjustable doctor knife of the micrometer type was used to cast dilute polymer solutions on Float Glass* using various knife-gap settings and casting solution concentrations to produce quite uniform dried films. The method is limited to films greater than 0.7 μ thickness, however, since films cast in this thickness range left what appeared to be casting lines on the surface due to the extremely fast evaporation of the acetone solvent. Solvents of slightly lower volatility may allow even thinner wet films to level before drying.

Data obtained with progressively thinner films, presented in Table 1, showed good salt retentions at modest product water fluxes. The films were heated on glass to 65°C before removal in water. With film thickness decreasing from 6.8 to 0.71 μ the product water fluxes increased from 0.58 to 12.9 gfd at 1500 psi. Salt retentions up to 98% were observed with both the thickest and thinnest films. The thinnest films (0.71 μ), however, showed increasing fluxes with time and eventual loss of most of their original salt retention even on 100 A pore diameter Millipore support.

This data indicated the need for improved mechanical properties to prevent degradation of the osmotic properties of thin films under reverse-osmosis conditions. It was postulated that the thin films might have extruded into irregularities in the surface of the support, forming thin spots which eventually ruptured and led to large increases in flux and salt permeation. Increasing the molecular weight of the polymer or heat-treating the thin film in the dry state (free from the glass plate) to increase its strength appeared to be the best means to improve the characteristics of the thin films. Poly(vinylene carbonate) of the highest molecular weight available** (804,000 mol wt) was evaluated, therefore, in the form of thin films. One film was evaluated without heat-treatment; the other film was heat-treated to 85°C for 0.5 hour after removal from the glass. Both films prepared from the polymer of higher molecular weight also showed the increase in flux and decrease in salt retention observed with the films of 0.71 μ thickness, although the extent of deterioration was somewhat less. Heat-treating the high molecular weight film in the dry form, free from the glass plate, apparently allowed the film to shrink slightly; this caused a decrease in the flux of the film, to about 50% of the flux of the unheated film, and an improvement in salt retention, from about 80% to about 90%. The effect of heat-treatment was not reflected in the

---

* Tin Float Glass produced by Pittsburgh Plate Glass.

** The monomer was first distilled from 1% sodium borohydride in a Vigreaux column, then distilled in a spinning band column at a 15:1 reflux ratio. Polymerization was conducted at 65°C without solvent in an evacuated and sealed ampoule using 0.093% of azobisisobutyronitrile (based on monomer)as the initiator.[1]

TABLE 1

THIN FILMS OF POLY(VINYLENE CARBONATE)

Run No.	Film Casting: Polymer,[a] %	Film Casting: Knife Gap, mils	Dried Film Thick., μ	Desalination (1500 psi - 3.5% NaCl Solution): Operating Hours[b]	Flux, gfd	Salt Ret., %	$D_1C_1 \times 10^7$ g/cm-sec	$D_2K \times 10^{10}$ cm^2/sec	D_1C_1/D_2K g/cm^3
1	10	5	6.8	8.5	0.70, 0.67	97.8, 96.9	- -	- -	- -
				20.5	0.65, 0.58	98.2, 97.1	3.82, 3.42	4.0, 5.5	960, 630
2	10	3	4.5	8.5	1.13 -	85.2 -	- -	- -	- -
				20.5	1.00 -	90.3 -	3.90 -	23 -	172 -
3	6.3	2	1.8	2.5	1.67, 2.25	95.7, 96.2	- -	- -	- -
				5.0	1.64, 2.16	96.1, 96.8	2.54, 3.37	5.7, 6.0	464, 562
4	6.3	1	1.2	1.5	2.11, 2.13	93.0, 92.1	- -	- -	- -
				5.0	2.15, 2.17	96.6, 95.4	2.09 -	4.0 -	523 -
5	3.5	1	0.76	3.2	3.9 -	94.5 -	2.57 -	8.0 -	322 -
				6.8	4.5 -	92.7 -	- -	- -	- -
				11.5	- Ruptured	- -	- -	- -	- -
6	3.5	1	0.71	1.0	2.0, 2.2	95.9, 97.2	- -	- -	- -
				6.2	4.2, 4.4	97.8, 98.0	2.58, 2.70	3.1, 3.0	834, 900
				17.2	9.9, 9.8	31.2, 32.8	- -	- -	- -
7	3.9	1	0.96[c]	1.7	7.0 -	80.7 -	- -	- -	- -
				2.7	6.1 -	84.1 -	- -	- -	- -
				4.1	6.8 -	79.1 -	- -	- -	- -
				20.8	12.9 -	52.1 -	- -	- -	- -
8	3.9	1	0.96[c,d]	1.9	3.0 -	88.9 -	- -	- -	- -
				3.0	3.3 -	90.4 -	- -	- -	- -
				4.3	3.2 -	91.4 -	- -	- -	- -
				5.4	3.2 -	92.2 -	- -	- -	- -
				22.3	7.5 -	78.7 -	- -	- -	- -

[a] Poly(vinylene carbonate) of 160,000 molecular weight in acetone unless otherwise noted.

[b] Millipore support of 1000 Å pore size was used in all Runs except Runs 5 and 6 in which 100 Å pore size support was used. Millipore Filter Corporation, Bedford, Massachusetts.

[c] Film was prepared from poly(vinylene carbonate) of 804,000 mol wt.

[d] Film was heat-treated in air at 85°C for 0.5 hr after removal from glass.

durability of the film, however, since both heated and unheated specimens showed partial failure at about the same operating time. It is possible that the use of a coarser support (1000 Å pore size) in place of the 100 Å pore dia support used previously contributed to the short life of the new films. However, it is felt that if the films had been dramatically improved, they would have held up over 1000 Å pore-size support. (For example, the osmotic properties of 0.24 μ thick films of cellulose acetate supported on 4500 Å Millipore support did not degrade over a 72-hour operating period.) It was concluded that higher molecular weight polymer and heat-treatment of the dry, free film may have increased the strength of the film but not enough to prevent eventual breakdown on 1000 Å pore size filter support under reverse-osmosis conditions.

The water permeability, D_1C_1, calculated from the reverse-osmosis data for the films of Table 1 was reasonably constant, ranging from 2.1×10^{-7} to 3.9×10^{-7} g/cm-sec vs about 1×10^{-7} g/cm-sec for cellulose acetate. This range compares quite favorably with values (reverse-osmosis data) obtained previously on much thicker poly(vinylene carbonate) films[1] and illustrates the potential flux advantage of poly(vinylene carbonate) over cellulose acetate.

The salt permeability values, D_2K, from the reverse-osmosis data are generally lower, indicating better salt retention than values obtained previously with thicker films.[1] The data overlap, but the lowest D_2K value (3.0×10^{-10} cm^2/sec) obtained here is about one-fifth of the lowest value obtained previously ($D_2K = 1.6 \times 10^{-9}$). The lower salt permeability values are probably a reflection of better operating techniques. The previous thicker films were tested in reverse-osmosis apparatus with relatively rough glass-fiber support plates which may have caused damage to the film by stretching over thickness irregularities.

A plot showing the expected linear relationship between flux and reciprocal film thickness of poly(vinylene carbonate) is presented in Figure 1. The flux values for each film were selected at maximum salt retention, and in most cases are averages of duplicates. It is assumed that the 100 Å pore dia of the filter supports used with the thinnest films (0.71 and 0.76 μ thick) did not limit the flux since 1000 Å pore dia filter support was used with the thicker films. This is borne out by the approximate linearity of the plot.

The ratios of the water permeability to salt permeability reached values as high as 960. This value is still only about one-half of the "theoretical value" (1800) calculated previously from the salt permeability determined by salt diffusion measurements[1] indicating that the films had imperfections. Therefore, efforts were directed toward the preparation of more perfect films by the plate withdrawal method of Carnell.[3]

ULTRATHIN FILMS

When it became apparent that thinner, more perfect films of poly(vinylene carbonate) were required than those produced by the knife-casting method,

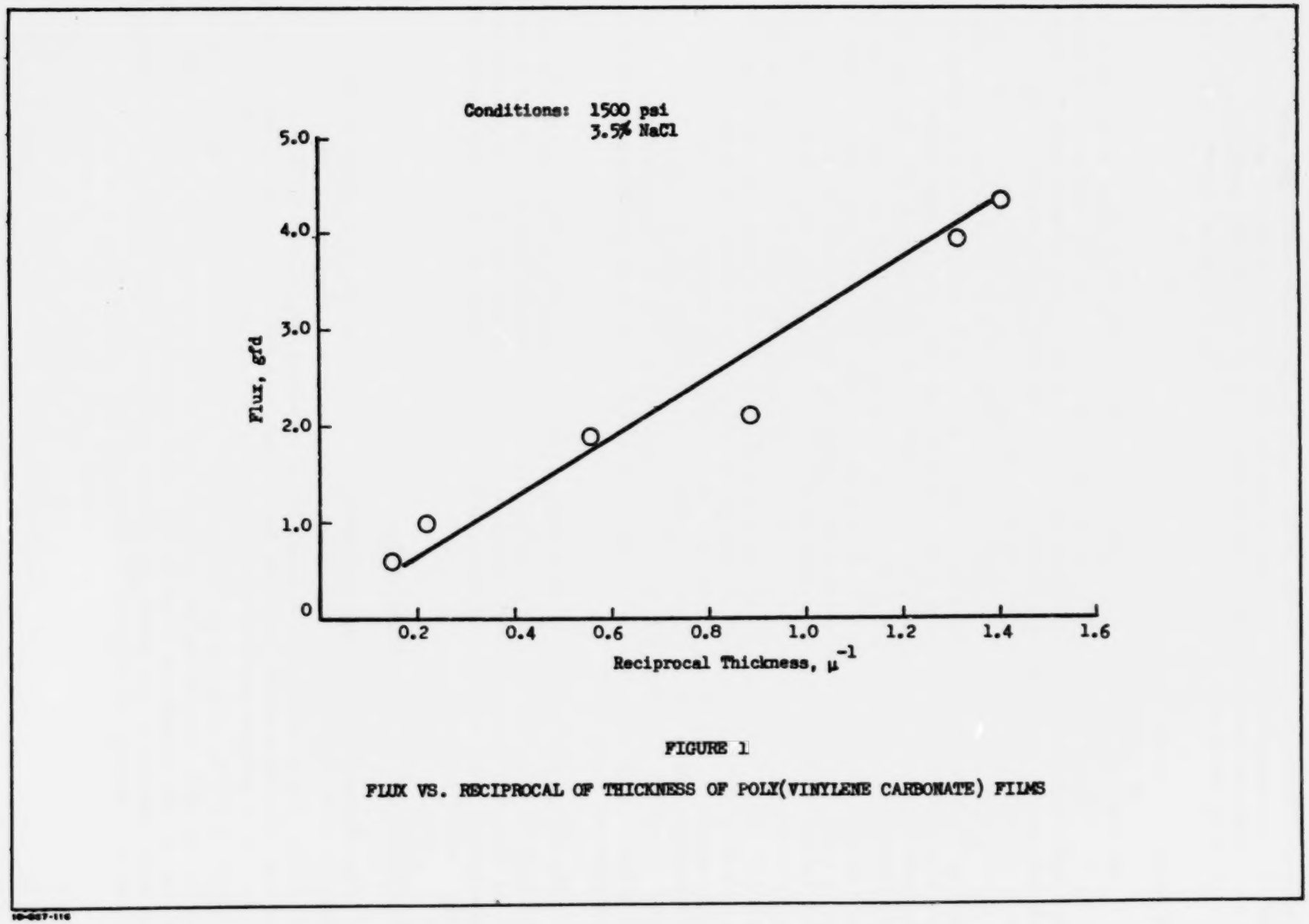

FIGURE 1

FLUX VS. RECIPROCAL OF THICKNESS OF POLY(VINYLENE CARBONATE) FILMS

a study of the technique of ultrathin film preparation was undertaken. An apparatus for preparing ultrathin films by the Carnell method[3] was constructed and cellulose acetate was employed initially to develop the necessary technique. The apparatus ultimately used to prepare ultrathin films is shown in Figure 2.

Apparatus

The container holding the polymer solution was made purposely tall to reduce air currents around the drawn, wet film. The glass plates were prepared from Float Glass, 0.25 in. thick and 3.5 in. wide, with seamed edges. This glass has an extremely smooth surface. A stainless-steel cable (1/32 in. dia - type 3 x 7 stranded) supporting the glass plate was passed over the 3/16-in. hub of the 7-in. pulley, then over a 4-in. pulley used to support the counter-weight away from the glass plate. The driving unit was a variable-speed motor mounted on a 1-in.-thick foam rubber pad to prevent the transmission of vibration to the apparatus. The 1-in. pulley on the motor shaft was connected to the 7-in. cable pulley by means of an 18-in.-dia rubber O-ring used as a belt. This O-ring also prevented vibration from reaching the cable. The casting plates could be withdrawn at speeds up to 9 in. per min; the lift speed, along with solution concentration, controlled the thickness of the ultrathin films. After the plate was raised, it, together with its attached air-dried film, was immersed briefly in water to plasticize the dried polymer. The seamed edges were scored by scraping with a knife, and the plate was reimmersed at an angle to float off the film on the surface of the water. The uniformity of the rate of plate withdrawal and freedom from vibration is reflected in the uniformity of the ultrathin film produced - other factors being equal. This apparatus gave ultrathin films of a single color, indicating uniformity of thickness.

The thickness of the film was controlled by varying the concentration of cellulose acetate in reagent grade acetone solution from 2.5 to 6.0%, and also by varying the lift rate from 1.2 to 9.0 in./min. Film thicknesses were determined by calculations based on the surface area and the dried weight of a sample of the film.

Ultrathin-Film Mounting Techniques

The ultrathin films were mounted on 3-in.-dia wet Millipore filters by floating the film over the filter which in turn was supported under water with a stainless-steel screen. Raising the screen and supported Millipore filter under the ultrathin film resulted in a smooth deposition of the film on the filter. This method resulted in the fewest wrinkles in the film. The film, Millipore support, and screen were allowed to dry in some cases before testing. This was thought initially to lend strength to the film and to facilitate mounting of the supported film in the test apparatus. Later, however, it was found that immediate wet mounting of the supported film gave the best results from the standpoint of film durability and salt retention.

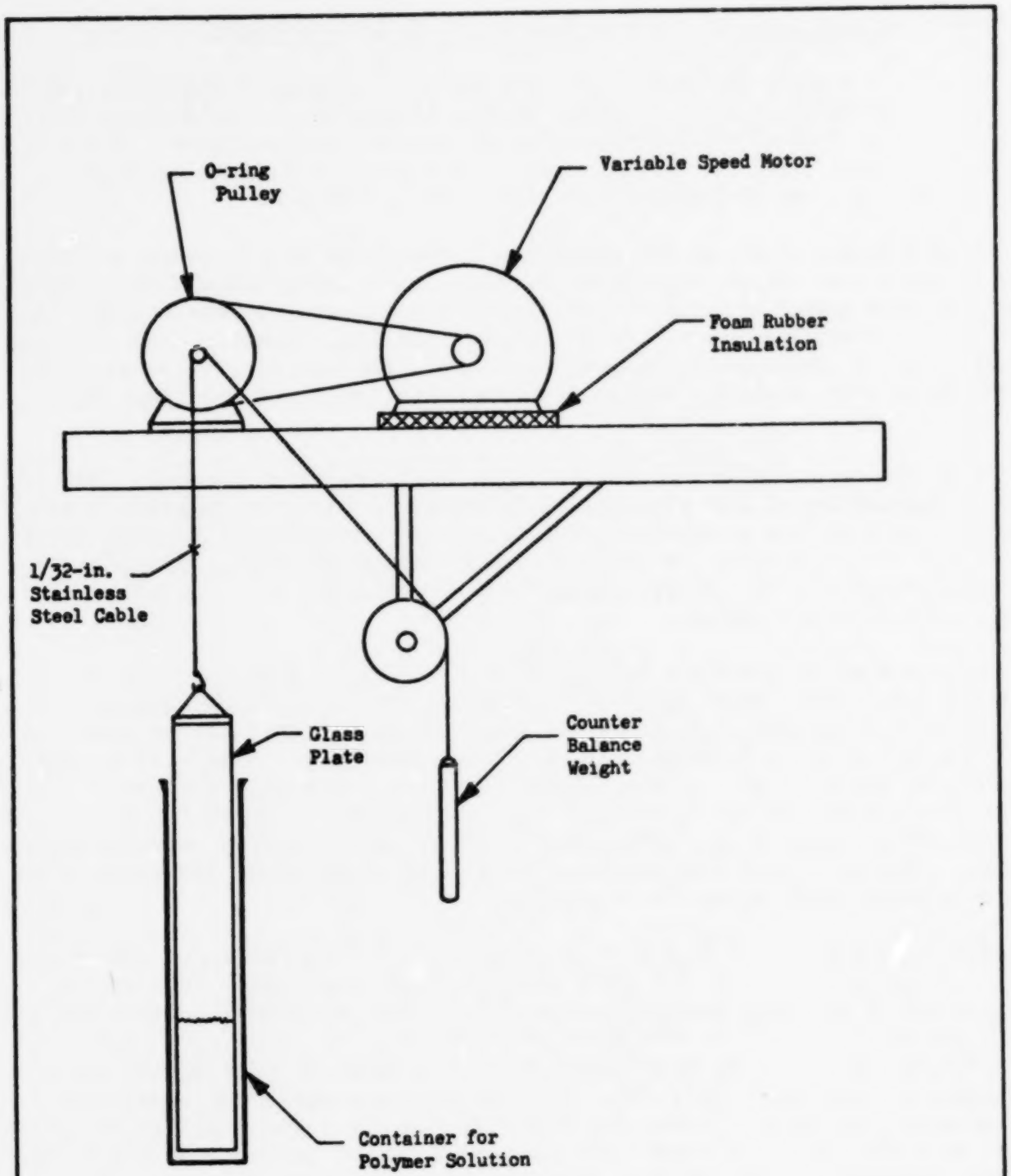

FIGURE 2

APPARATUS FOR THE PREPARATION OF ULTRATHIN FILMS

Procedures for the Reverse-Osmosis Testing of Ultrathin Films

It was necessary to develop new procedures for supporting ultrathin films in the reverse-osmosis cell and start-up procedures which would apply the hydraulic force smoothly and prevent damage to the fragile films. The evaluation of ultrathin films of cellulose acetate and the modification in the film mounting and start-up procedures are presented in Table 2.

Approximately half of the ultrathin films which were mounted on Millipore supports and dried before testing either developed leaks, showed evidence of small pin holes after testing, or ruptured during test. It was thought that most of these breakdowns were the result of handling, clamping, and start-up techniques which physically damaged the films. The better results with wet-mounted films were probably due in part to better handling and start-up techniques.

With Run No. 1, shown in Table 2, the salt retention was only 92.6 to 94.8%. Examination of the supported film revealed that the relatively rough surface texture of the glass-fiber support plate was embossed through the paper support and onto the film. Relatively smooth stainless-steel porous plates were substituted for the porous glass-fiber plates, and the embossing effect was not a problem thereafter.

A relatively thick film (11,400 Å) was tested in Run No. 2 and allowed to run for 46 hours. Salt retention increased with time along with decreasing product water flux, and this trend was demonstrated in most of the subsequent runs. Run No. 3 (2420 Å thick film) was made to evaluate higher flux rates and to obtain an estimate of the rate of flux decline. The salt retention (97.3%) was not as high as the 99.1% obtained with the thicker film of Run No. 2. The flux held up well, however, showing only 2.8 gfd decline over approximately 72 hours. The salt retention held up quite well in spite of the relatively large pore size (4500 Å) of the support.

With the use of 500 Å Millipore support, the film thickness was reduced to 756 Å (Runs No. 4 and 5) to study still higher flux rates. Run No. 4 exhibited about the same salt retention (97.5%) as the previous films but flux decline was more severe, amounting to a decrease of 5.5 gfd in 24 hours. It was expected also that the flux would be in the range of 30 from the relative thicknesses of the two films. The finer Millipore support may thus have restricted product water flux. The film for Run No. 5 was dried 10 min before removal from the plate. It was more difficult to remove from the plate and may have been damaged during removal, possibly accounting for the low retention. Runs No. 6 and 7 were evaluated to determine the orientation effect of the Millipore support. Little difference in flux or salt retention was noticed when the 500 Å pore size filter support was mounted with the dull side or the shiny side up.

TABLE 2

ULTRATHIN FILMS OF CELLULOSE ACETATE[a]

Run No.	Film[b] Thickness, Å	Film Support[c] Pore Size, Å	Orientation	Support Plate	Testing (1500 psi - 3.5% NaCl Solution) Startup Procedure[d]	Operating Hours	Flux, gfd	Salt Ret., %
1	2,540	4500	Shiny side up	Glass fiber	Reg start	3.5	12.0	92.6
						20.0	7.0	94.8
2	11,400	4500	Shiny side up	SS porous		1.3	1.4	95.3
						19.7	1.2	98.9
						46.3	1.2	99.1
3	2,420	4500	Shiny side up			0.5	12.8	96.1
						6.0	12.0	97.3
						41.0	10.0	97.5
						72.0	10.0	97.3
4	756	500	Dull side up[e]			0.5	21.0	85.2
						1.5	19.0	97.5
						4.5	18.0	97.7
						24.0	15.5	97.5
5	756	500	Dull side up[f]			2.0	19.0	89.4
						7.0	17.0	90.9
6	5,480	500	Dull side up			1.0	3.0	94.1
						19.5	2.7	97.6
7	5,480	500	Shiny side up		Reg start	0.5	2.8	97.4
						17.5	2.8	98.1
8	3,910	500	Dull side up	SS porous	Easy start[g]	0.5	8.1[h]	94.8[h]
						23.0	5.5[h]	98.0[h]

[a] Eastman E 398-3 cellulose acetate.

[b] Film prepared by Carnell method of plate withdrawal from acetone solutions of cellulose acetate.

[c] Millipore filter media on No. 50 Whatman paper. "Orientation" shows which surface of the filter was against the membrane ("up"). Ultrathin film mounted wet on Millipore and allowed to dry before desalination test except in Runs 7 and 8 in which the films were tested without drying.

[d] Regular start from zero hydraulic feed pressure using the hydraulic pump.

[e] Ultrathin film removed from glass plate within 90 sec of withdrawal from coating solution.

[f] Ultrathin film dried 10 min before removal from glass plate.

[g] Easy start employed N_2 gas pressure on feed solution through accumulator diaphragm to raise pressure slowly to 1500 psi followed by startup of hydraulic pump.

[h] Average product water flux and salt retention of three circles run at the same time.

It was noted during these runs that the film sometimes ruptured shortly after start-up of the hydraulic pump.* This was apparently caused by back pressure developed on the return stroke of the pump piston at low pressures. Such back pressure tends to lift the film from the support and often results in rupture. At higher pressures, this effect was not observed. A new start-up procedure was developed to obviate the back-pressure difficulties and to afford a smoother, initial pressurization of the unit. All gas pressure was released from the bladder type accumulator, and the pump was operated at essentially zero pressure to fill the unit with feed solution and drive out any air. This also depressed the bladder of the accumulator slightly. The pressure-reducing recycle valve was then closed and the accumulator pressurized on the gas side with nitrogen nearly to the operating pressure. The gas pressure was transmitted smoothly through the bladder as hydraulic pressure, and the pump was then started to maintain hydraulic pressure and recirculate the feed solution.

The new start-up procedure was used with Run No. 8 in which the salt retentions (98%) and product water fluxes (5.5 gfd at 23 hours) are averages of three films run at the same time. None of these films broke during the start-up; the run, however, was terminated after 23 hours because of power failure.

With the successful development of the procedure for preparing ultrathin films of cellulose acetate, full attention was turned to application of the procedure to poly(vinylene carbonate) as described in the following section.

Ultrathin Films of Poly(vinylene carbonate)

The ultrathin films of poly(vinylene carbonate) were prepared in a manner similar to that used for cellulose acetate. Poly(vinylene carbonate), however, is slightly adhesive toward glass, and the ultrathin films were more difficult to remove from the glass plates. Because of this, it was difficult to prepare films from polymer of 160,000 mol wt which were thinner than 3700 Å. Films from this polymer were not heat-treated on glass since it was felt this treatment might increase adhesion. In general, films of 160,000 or 400,000 mol wt did not hold up as well under test as cellulose acetate films of comparable thickness.

Poly(vinylene carbonate) films 9 and 10 of 3740 Å thickness in Table 3 were evaluated on 4500 Å Millipore filter. These films ruptured after 1 hour of operation, probably because of the large pore size of the Millipore support. Films No. 11 and 12 of 6000 Å thickness mounted on 500 Å Millipore showed increasing product water flux during 5.1 hours operation. The salt retention reached a maximum of 88.3% with a flux of 10 gfd at 4.5 hours of operation. Thereafter the flux increased and the salt retention decreased.

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* An air-driven piston pump (Model S440-35CS-SS, Sprague Engineering Company of Gardena, California) was used in this work.

TABLE 3

ULTRATHIN FILMS OF POLY(VINYLENE CARBONATE)

Film[a]				Desalination Test (1500 psi - 3.5% NaCl)		
Run No.	Thickness, Å	Mol Wt	Support Pore Size, Å	Operating hours	Flux, gfd	Salt Retention, %
9[b], 10[b]	3740	160,000	4500[c]	0.5	18.0, 13.0 -	56.2, 70.4 -
				1.0	Ruptured	- - -
11[b], 12[b]	6000	160,000	500[c]	0.5	7.0, 4.0 -	53.0, 59.0 -
				4.5	12.0, 10.0 -	79.1, 88.3 -
				5.5	16.5, 14.0 -	69.2, 86.4 -
13[d], 14[d], 15[d]	5000	400,000	1000[e]	3.3	8.5, 6.4, 6.6	83.0, 85.5, 78.5
				4.5	7.5, 5.5, 6.0	86.2, 89.3, 83.8
				10.5	10.7, 8.9, 8.4	78.5, 86.3, 87.0

[a] Films drawn from acetone solution of polymer by the Carnell method.[3]

[b] Film mounted wet on support and allowed to air-dry before testing. Regular Sprague pump start.

[c] Millipore filter medium.

[d] Film mounted wet on support and tested without drying. Easy startup procedure used.

[e] Metricel filter medium (cellulose triacetate).

Poly(vinylene carbonate) of higher molecular weight (400,000) was evaluated for the preparation of ultrathin films with improved strength. A 6% solution in dimethylformamide used at a lift rate of 6.7 in./min gave wet films which dried very slowly. Because of this, the wet film receded from the edges toward the center of the plate during drying and none of the films was suitable for use. Fortunately, it was found that polymer of this molecular weight was soluble in acetone to the extent of 5.5%. Films (13, 14, and 15) of 5000 Å thickness pulled from this solution at 6.7 in./min lift rate were of good quality and appeared to be stronger than those of 160,000 mol wt. The reverse osmosis data indicated that they were somewhat more durable in that the rate of flux increase was not as great. However, after passing through a maximum, the desalination fell off with increasing flux indicating a breakdown in the film. The increase in flux and a maximum in the salt retention during flux increase for Runs 11 through 15 parallels the data obtained with thin knife-cast poly(vinylene carbonate) films (Table 1, Run No. 6). The lower salt retention properties of ultrathin films compared with those of knife-cast films (Runs 5 and 6, Table 1) may have been caused by more than simply the film thickness. The thin films were heated to 65°C, and this heat-treatment may have strengthened them.

It was postulated that the poly(vinylene carbonate) films (thin knife-cast and ultrathin) may have extruded into the pores of the support forming thin spots on the film which eventually ruptured and led to increases in flux and salt permeation. At this point, it appeared desirable to compare the mechanical properties of poly(vinylene carbonate) and cellulose acetate in an effort to explain the failure of thin films of poly(vinylene carbonate) when tested over an extended period at 1500 psi.

MECHANICAL PROPERTIES

The mechanical properties of poly(vinylene carbonate) and cellulose acetate film were compared in an effort to understand the failure of ultrathin films of poly(vinylene carbonate) under reverse-osmosis conditions. The tensile properties of poly(vinylene carbonate) and cellulose acetate films, determined under water, showed that, although poly(vinylene carbonate) films have a greater ultimate tensile strength and yield point, they are stiffer and more brittle than cellulose acetate films. The latter films are more ductile, much tougher, and undergo plastic deformation more readily under stress. Brittleness appears to be the main factor which contributes to the failure of thin and ultrathin films of poly(vinylene carbonate) under reverse-osmosis conditions.

A film of cellulose acetate was prepared by casting a 10-mil wet thickness on glass from a 22% cellulose acetate* solution in acetone. After drying at 60°C overnight, the film was removed from the glass plate by soaking in deionized water; the thickness was 1.05 mils. A poly(vinylene carbonate) film was prepared by casting a 10-mil thickness of a 12.7% poly(vinylene carbonate) (485,000 mol wt) solution in dimethylsulfoxide on a glass plate.

* Eastman E 398-3 cellulose acetate.

After oven drying at 60°C overnight, the film was removed from the glass plate by soaking in deionized water; the film's thickness was 0.70 mils. Tensile specimens 0.506-cm wide and 30-cm long were cut under water by means of a double-bladed strip cutter. The tensile measurements were made using the procedure developed previously[4] and the crosshead speed and chart speed for the Instron Instrument were adjusted to give the best curve for these films. The data presented in Table 4 were obtained using a 0.05 in./min crosshead speed and a chart speed of 2.0 in./min. From the average values of the tensile properties, it is evident that the elastic modulus, yield point and ultimate tensile strength of poly(vinylene carbonate) is much higher than that for cellulose acetate films. The higher elastic modulus of poly(vinylene carbonate) shows that it is stiffer than cellulose acetate. The yield point and tensile strength of the poly(vinylene carbonate) are also higher than those of cellulose acetate, but the elongation at yield and break for the former are lower. Cellulose acetate exhibits nearly 10 times greater elongation at break than poly(vinylene carbonate). The greater stiffness and much lower elongation at break of poly(vinylene carbonate) indicate that this material is quite brittle compared to cellulose acetate.

Although cellulose acetate is not as strong as poly(vinylene carbonate) with respect to resistance to plastic deformation or resistance to the force necessary to rupture the film, it is tougher and can absorb more energy and sustain more deformation before rupture. It does this by undergoing plastic deformation under the forces which would eventually split or crack a more brittle material. These differences are illustrated by the stress-strain curves (Figure 3) for specimen 1 of poly(vinylene carbonate) and specimen 2 of cellulose acetate from Table 4. The ratio of the total areas under the two curves is approximately 9 to 1. Thus, cellulose acetate has about 9 times greater toughness than poly(vinylene carbonate). However, the latter is the more resilient (can absorb more energy before undergoing plastic deformation), since it has the greater area (ratio 1.3 to 1) under the curve within the elastic limit (the yield point).

From this evaluation of the tensile data of both materials, it appears that the failure of thin and ultrathin films of poly(vinylene carbonate) is directly related to their brittleness. Thus, thin films of the polymer tend to rupture when forced against even minute surface irregularities in the supporting layer during reverse-osmosis tests. Cellulose acetate can more easily undergo plastic deformation, can flow into surface irregularities, and can resist rupture even though its ultimate tensile strength is less. Therefore, it was concluded that modification of poly(vinylene carbonate) to provide greater elongation would be required to eliminate the loss of salt retention during operation under pressure. This might be accomplished by plasticizers with the loss of some of the tensile strength or by incorporation of comonomers. The program conducted on copolymerization is described in the following section.

TABLE 4

TENSILE PROPERTIES OF POLY(VINYLENE CARBONATE)
AND CELLULOSE ACETATE FILMS UNDER WATER

Film Type	No.	Elastic Modulus $kg/cm^2 \times 10^{-3}$	Yield Point kg/cm^2	Tensile Strength kg/cm^2	% Elongation Yield	% Elongation Break
PVCarb	1	28.0	325	325	1.62	1.79
	2	30.0	329	334	1.46	1.62
	3	29.1	304	304	1.41	1.53
Average		29.0	319	321	1.50	1.65
CA	1	18.0	212	204	1.78	16.1
	2	17.4	204	204	1.73	17.3
	3	15.8	205	224	1.82	19.3
	4	18.2	206	195	1.68	14.7
Average		17.4	207	207	1.75	16.9

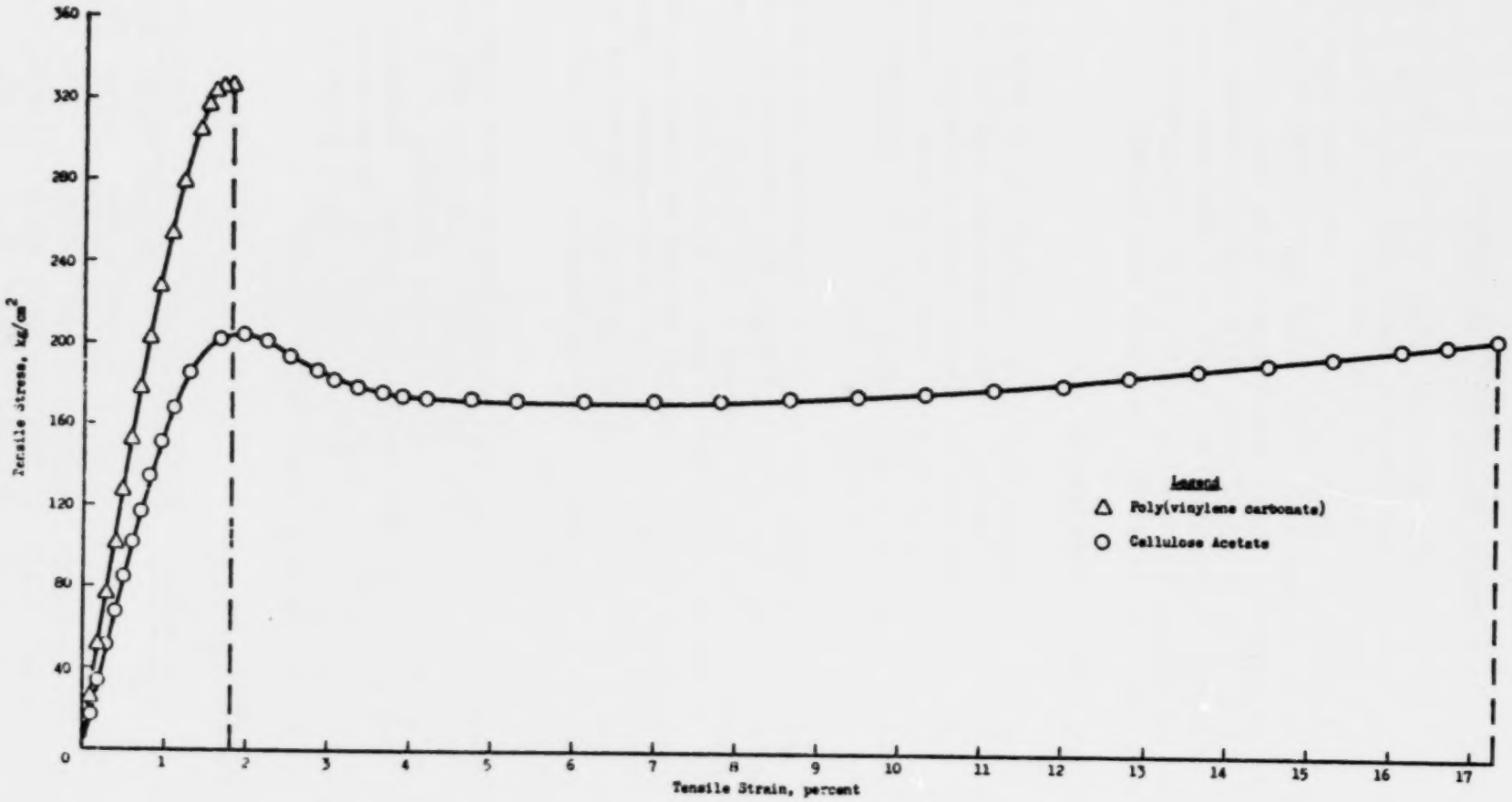


FIGURE 3

TENSILE STRESS-STRAIN CURVES FOR POLY(VINYLENE CARBONATE) AND CELLULOSE ACETATE FILMS

COPOLYMERS BASED ON VINYLENE CARBONATE

Vinylene carbonate has been copolymerized with several comonomers by other investigators. The low copolymerization reactivity rates of vinylene carbonate, however, limits the selection of comonomers. Two of the best comonomers from this standpoint are vinyl acetate and vinylpyrrolidine. Fortunately, both have polar groups and, thus, both may contribute to the osmotic properties of copolymers. Vinyl acetate has been used as a comonomer to provide increased plasticity in copolymers with vinyl chloride, methacrylate, and styrene.[5] Vinyl acetate, therefore, was used as a comonomer with vinylene carbonate in an effort to obtain internally plasticized copolymers that exhibit properties more plastic than the vinylene carbonate homopolymer.

VINYLENE CARBONATE/VINYL ACETATE COPOLYMERS

Copolymers of vinylene carbonate with vinyl acetate have been prepared in acetone solution by Hayashi and Smets;[6] their comonomer reactivity ratios, r_1 and r_2, were 0.27 and 3.0, respectively. Other workers obtained values of 0.15 and 4.0, respectively, for polymerization without solvent.[7] Thus, it was expected that vinyl acetate would be incorporated into the copolymer in a greater mole ratio than that of the monomer mixture.

The 5/1, 3.3/1 and 1.6/1 mole-ratio vinylene carbonate/vinyl acetate copolymers were prepared from the purified monomers for evaluation. The vinylene carbonate monomer was distilled through a spinning-band column as described previously.[1] A second distillation was conducted with 1.0% sodium borohydride in the distillation pot as a further method of removing any dichloroethylene carbonate impurity that might be present in the monomer. The vinyl acetate monomer supplied with 3 to 5 ppm of hydroquinone inhibitor* was mixed with cuprous oxide powder** (J. T. Baker Chemical Company) for distillation at 39-41°C under reduced pressure before use.

The vinylene carbonate and vinyl acetate comonomers were mixed with the desired amount of azobisisobutyronitrile (AIBN) initiator, and the mixture was sealed under vacuum in a small ampoule. The ampoule was held in an oven at 65°C for 3 days, and was then removed, cooled, and opened. The reaction mixture was dissolved in dimethylsulfoxide, precipitated in methanol, washed, and dried overnight in a vacuum oven at 60°C to yield the copolymer. Pertinent data are tabulated below for the copolymer preparations.

	Comonomers								
	Vinylene Carbonate		Vinyl Acetate		AIBN Initiator		Copolymer		
Copolymer No.	Wt g	Mole%	Wt g	Mole%	Wt g	Wt%***	Yield Wt%	VC/VA Ratio	Specific Viscosity****
71	31.2	0.97	0.93	0.03	0.0325	0.100	27.0	5/1	0.75
88	31.2	0.87	4.65	0.13	0.0377	0.105	19.6	1.6/1	0.45
98	31.2	0.92	2.80	0.08	0.0243	0.069	21.0	3.3/1	0.64

* By Monomer-Polymer Laboratories, The Borden Chemical Company, Philadelphia, Pennsylvania.
** A polymerization inhibitor.
*** Based on total monomer weight.
**** 0.08% in acetone at 25°C.

The relatively low specific viscosity of the 1.6/1 copolymer indicates that its molecular weight is lower than that of either the 5/1 or the 3.3/1 copolymer.

The relative amounts of the comonomers incorporated into the copolymers in the foregoing tabulation were calculated from the elemental analyses shown below.

	Wt%		
	C	H	O (by Difference)
Poly(vinylene carbonate)	39.85	2.62	57.53
Copolymer 71	42.48	3.08	54.44
Copolymer 88	46.00	4.35	49.65
Copolymer 98	43.65	3.68	52.67
Polyvinyl acetate (theoretical)	55.82	6.98	37.20

The mole ratios of the comonomers incorporated into the copolymers were determined from a linear plot of these data.

Infrared spectrograms of the copolymer films and the vinylene carbonate homopolymer are presented in Figure 4. As more vinyl acetate is incorporated into the copolymer, the >C=O band of the acetate group at 5.77 μ becomes more intense, approaching the intensity of the >C=O band of the carbonate group at 5.53 μ.

The copolymers of vinylene carbonate and vinyl acetate were readily soluble in reagent-grade acetone, and casting solutions containing up to 15% copolymer were made for the preparation and evaluation of films.

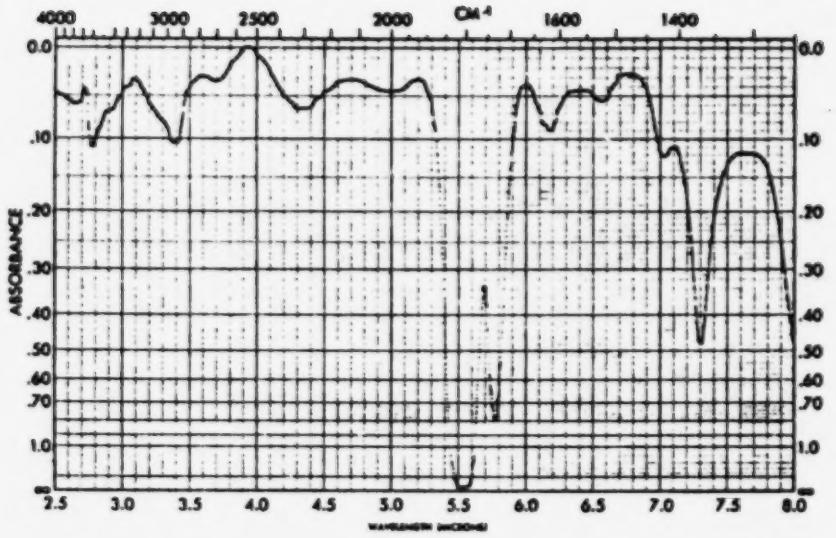
Tensile Properties of Copolymers

The tensile properties of films of vinylene carbonate/vinyl acetate copolymers were determined under water at 25°C and compared with the tensile properties of the vinylene carbonate homopolymer and cellulose acetate.

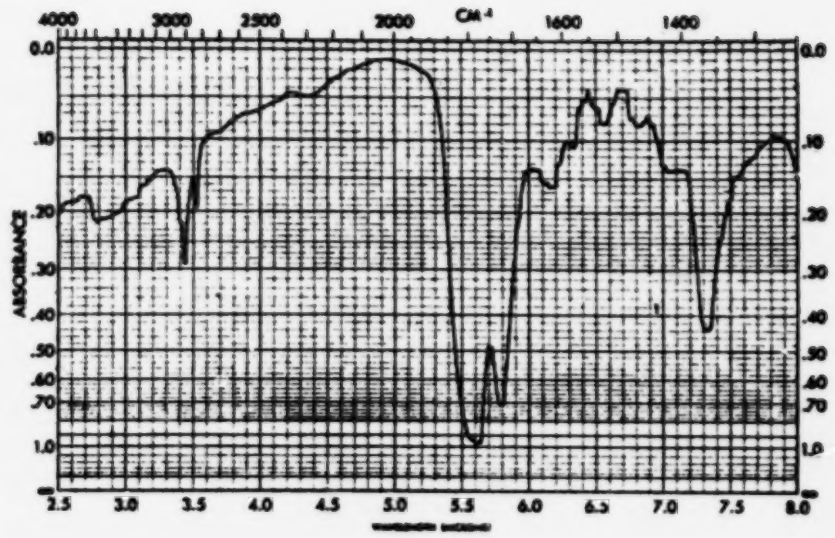
The copolymer films were prepared by casting a 10-mil thickness of the 15% copolymer solution in acetone on glass plates. After overnight drying at 60°C, the films were removed from the plates by soaking in deionized water.

Tensile specimens, 0.506 cm wide and 30 cm long, were cut under water with a double-bladed strip cutter. The tensile measurements were made with a 0.05-in./min crosshead speed and a chart speed of 2.0 in./min using a procedure developed previously.[4]

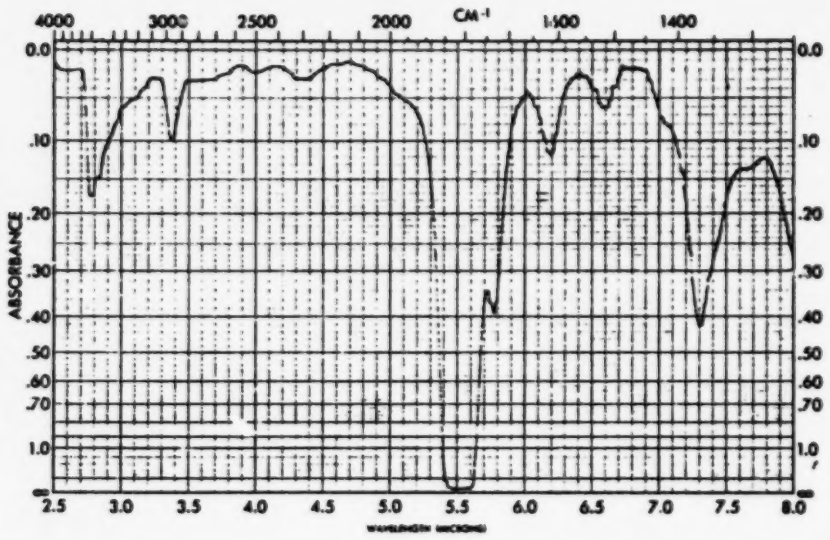
The tensile properties of vinylene carbonate/vinyl acetate copolymer films are presented in Table 5 along with those for the vinylene carbonate homopolymer and cellulose acetate. The elastic moduli of the 5/1 and the 3.3/1 mole-ratio vinylene carbonate/vinyl acetate copolymers were higher



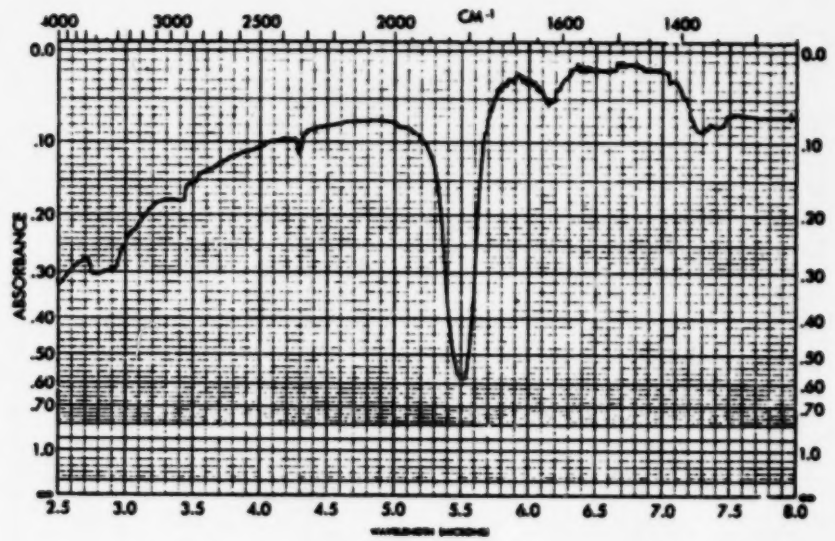
A. 1.6/1 Copolymer



B. 3.3/1 Copolymer



C. 5/1 Copolymer



D. Vinylene Carbonate Homopolymer

Figure 4 Infrared Spectrograms of Vinylene Carbonate/Vinyl Acetate Copolymers and Vinylene Carbonate Homopolymer

TABLE 5

MECHANICAL AND REVERSE-OSMOSIS PROPERTIES OF COPOLYMER FILMS

Film	Tensile Properties[a]					Desalination (at 1500 psi, 3.5% NaCl Feed Solution)			
	Modulus $kg/cm^2 \times 10^{-3}$	Yield kg/cm^2	Break kg/cm^2	Elongation, % Yield	Elongation, % Break	Thickness mils	Water Flux gfd	Salt Retention %	Calc. Flux (gfd) for a 2500-Å-Thick Film
VC/VA copolymer (5/1 mole ratio)	32.0 ±1.4[b]	-	330 ±30	-	1.2 ±0.7	0.36	0.35	84	12.8
VC/VA copolymer (3.3/1)	32.6 ±0.6	-	210 ±18	-	0.75 ±0.04	0.60	0.03	71	1.8
VC/VA copolymer (1.6/1)	23.8 ±0.6	262 ±2	262 ±2	1.34 ±0.05	1.42 ±0.05	0.30	0.052	65	1.6
Poly(vinylene carbonate	29.0 ±0.6	319 ±8	321 ±9	1.50 ±0.06	1.65 ±0.08	0.27	0.62	98	17.0
Cellulose acetate[c]	17.4 ±0.5	207 ±2	207 ±6	1.75 ±0.03	16.9 ±0.98	-	-	-	10-12

[a] Determined in water with a crosshead speed of 0.05 in./min as described previously.

[b] Standard deviation of the mean, $S_{\bar{x}} = \pm \sqrt{\frac{(\Sigma(d)^2}{n\,(n-1)}}$.

[c] Eastman Kodak E 398-3.

than that for the vinylene carbonate homopolymer, and the elongations at the break point were less. This indicates a stiffer, less-elastic material that is more brittle than the homopolymer. The incorporation of vinyl acetate comonomer into the vinylene carbonate/vinyl acetate copolymer thus has an anti-plasticizing effect instead of the desired plasticizing effect. This phenomenon has been demonstrated by others with bisphenol polycarbonates.[8] In attempts to plasticize these polymers, several antiplasticizers such as poly(styrene glycols) gave stiffer materials with lower elongation at the break point. The intermolecular forces, which in part determine the mechanical properties, are apparently reinforced instead of being dissipated as in normal plasticization. It therefore appears that the incorporation of vinyl acetate comonomer into the vinylene carbonate/vinyl acetate copolymer effects a reinforcement of the intermolecular forces with the 5/1 and 3.3/1 copolymers (17 and 23 mole % vinyl acetate, respectively).

The 1.6/1 vinylene carbonate/vinyl acetate copolymer exhibited a lower modulus and lower yield and break points than the vinylene carbonate homopolymer, but its elongation was still less than that for the homopolymer. These findings show that the copolymer is not as stiff or strong as the vinylene carbonate homopolymer. The appearance of a yield point, however, indicates incipient plasticization but not to the point of increasing the elongation of the material. The plasticity of cellulose acetate is still far greater, as is evident from the mechanical-property values given in Table 5.

Osmotic Properties of Copolymers

Reverse-Osmosis Test

The relationships between the reverse-osmosis properties of films of the copolymers of vinylene carbonate and vinyl acetate are also presented in Table 5. Copolymer films for reverse-osmosis testing were prepared with the same casting solutions that had been used for specimens subjected to mechanical-property testing, except that they were made much thinner.

As more vinyl acetate is incorporated into the vinylene carbonate/vinyl acetate copolymer (38 mole % vinyl acetate in the 1.6/1 copolymer), both the salt retention and the flux (calculated at a film thickness of 2500 Å) decrease. The salt-retention decrease appears to be linear with the number of acetate groups substituted for vinylene carbonate groups. The flux, however, is decreased to approximately one-tenth the flux of the vinylene carbonate homopolymer. The vinyl acetate apparently interferes with water transport through the membrane.

Salt Permeability of Copolymers

The salt permeabilities of vinylene carbonate/vinyl acetate copolymer films were investigated by the electrical-conductivity method.[9] The films were prepared in a dry box under controlled conditions, because anomalous results had been obtained with some films prepared outside the dry box under

ambient conditions. Two films of a 5/1 mole-ratio vinylene carbonate/vinyl acetate copolymer were cast and dried in a dry nitrogen atmosphere. They were prepared in a 5-mil wet thickness from a 15% solution of the copolymer in acetone. The dried films were removed from the glass plate by immersion in deionized water and were equilibrated with water for 24 hours before testing. The salt-diffusion coefficients (D_2) and the salt-distribution coefficients (K) shown below were determined for the 2 films by the electrical-conductivity method, using a 1-molar sodium chloride solution.

Film Thickness, mils	D_2 cm^2/sec	K	D_2K cm^2/sec
0.40	8.26×10^{-11}	0.32	2.62×10^{-11}
0.35	4.90×10^{-11}	0.58	2.85×10^{-11}

The salt permeabilities (D_2K) obtained for the 5/1 copolymer are about one-tenth the previous values obtained for vinylene carbonate homopolymer by the immersion method[1] ($D_2K = 2.6 \times 10^{-10}$, $K = 0.24$). Because the latter film was prepared under ambient conditions outside a dry box, the comparison may not be valid.

Initial films from the 1.6/1 vinylene carbonate/vinyl acetate copolymer were prepared outside the dry box under conditions of relatively high humidity. They gave very low electrical resistances, indicating that casting and drying at relatively high humidity may have caused a porous structure. As the acetone evaporates from wet cast films, the temperature of the film surface can fall below the dew point of the surrounding air and condense water vapor onto the film. This condensation could cause polymer precipitation in the film, leading to a partially porous structure.

Other films of the 1.6/1 copolymer were prepared in the dry box under a nitrogen atmosphere in the same manner as the 5/1 copolymer. Initially, the electrical resistances of these water-equilibrated polymers showed an increase with time, reached a peak, and then slowly fell over a 4-day period. An equilibrium resistance was not reached in a reasonable length of time, however, and the salt permeability (D_2K) could not be calculated. The initial increase in film resistance cannot be explained. It may possibly be associated with an initial osmotic loss of water when the water-equilibrated film is immersed in the 1-molar salt solution in the conductivity cell.

For further study of this phenomenon, vacuum-dried films of the 3.3/1 copolymer were tested against 1-molar salt solution to eliminate any initial osmotic loss of water from the film. These dry-mounted films gave extremely high resistances (2,500,000 ohms) over a 48-hour period with no evidence of change. Such resistances suggested that the anhydrous films excluded water as well as salt. On the other hand, the films that were water-equilibrated before mounting in the conductivity cell did not exclude salt so efficiently, presumably because of the prior presence of water.

Whether this phenomenon is peculiar to copolymer films or is also associated with other dried films (such as cellulose acetate) is not known. In any event, the salt-permeability study indicates the importance of preparing films under controlled conditions in the absence of excessive water vapor. Films prepared under the best conditions to give the lowest D_2K values would also be expected to have the best properties in reverse-osmosis testing.

VINYLENE CARBONATE/VINYLPYRROLIDONE COPOLYMERIZATION STUDIES

The copolymerization of vinylene carbonate and N-vinyl-2-pyrrolidone was studied in attempts to obtain internally plasticized copolymers that would not be as brittle as the poly(vinylene carbonate) homopolymer. The copolymerization of vinylpyrrolidone with vinylene carbonate has been carried out by K. Hayashi[6] in acetone solution at 60°C, using azobisisobutyronitrile (AIBN) as the initiator. Hayashi found that both the rate of reaction and copolymer yield fell off as the proportion of vinylene carbonate monomer in the mixture was increased. At a 9/1 molar ratio of vinylene carbonate to vinylpyrrolidone, the copolymer yield was only 5.5 mole %. Therefore, the copolymerization studies on this program were conducted in bulk, rather than in acetone solution, in hopes of increasing the copolymer yield. This work is an extension of the previous work with vinyl acetate as comonomer in attempts to obtain an internally plasticized vinylene carbonate-vinyl acetate copolymer. In those studies, it was only necessary to purify the vinyl acetate by a simple distillation under reduced pressure to obtain copolymer grade vinyl acetate monomer. N-vinyl-2-pyrrolidone* proved to be more difficult to copolymerize with vinylene carbonate, as is shown by the following polymerization data:

Vinylene Carbonate, g	Vinyl-pyrrolidone, g	AIBN Catalyst, g	Polymerization
33.2	5.3**	0.026	none
-	10.6***	0.004	polymer
31.2	5.3***	0.038	none
31.2	1.0***	0.033	none
31.2	1.0****	0.056	none
31.2	-	0.024	polymer
37.7	-	0.029	polymer
31.2	-	0.024	polymer

The vinylene carbonate was distilled from 1% sodium borohydride in a Spinning band column at a 10/1 reflux ratio. The homopolymers, polyvinylpyrrolidone and poly(vinylene carbonate), in each case were prepared readily when initiated in bulk with AIBN catalyst at 65°C. However, none of the comonomer mixtures polymerized, even when the vinylpyrrolidone was further

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* Monomer-Polymer Laboratories, The Bordon Chemical Company, Philadelphia, Pennsylvania.

** Simple Vigreaux distillation.

*** Distillation from a spinning band column at a 10/1 reflux ratio.

**** Double spinning band distillation (heart cut redistilled).

purified or its proportion was reduced. This indicated that the impurities still present in the distilled sample of vinylpyrrolidone would not prevent homopolymerization, but would prevent copolymerization with vinylene carbonate comonomer. The three batches of poly(vinylene carbonate) homopolymer were combined in DMSO solvent; were reprecipitated, washed, and dried; and were used later in external plasticizer experiments.

POLY(DIACETONE ACRYLAMIDE)

Poly(diacetone acrylamide) was evaluated as a new membrane material because of several promising properties. These properties are (a) the hydrophilic nature of the polymer, (b) good water sorption, (c) favorable water-vapor transmission rates, (d) excellent hydrolytic stability (stable to 50% aqueous sodium hydroxide for 24 hours), (e) an apparent glass transition point at 84°C, and (f) the ability to be crosslinked. The polymers are insoluble in water, and both the water sorption and solubility in a wide variety of solvents, including ketones, are dependent on the molecular weight of the polymer. The adhesive properties and the rather elastic nature of poly(diacetone acrylamide) when plasticized with water presented problems in its use in thin films.

POLYMERIZATION

Diacetone acrylamide* was polymerized in water at room temperature in yields over 95% using a redox catalyst. In a typical polymerization the monomer was dissolved in distilled water in a 3-necked round-bottom flask equipped with a combination nitrogen inlet-catalyst addition tube, a stirrer, a thermometer, and a nitrogen bubble tube to indicate the gas flow rate. Nitrogen was bubbled through the monomer solution for 0.5 hour to remove air. The polymerization was initiated by addition of an aqueous solution of ammonium persulfate followed by an aqueous solution of sodium bisulfite. After 2 hours, 10 ml of concentrated hydrochloric acid was added with stirring and the polymer was then filtered off, water-washed, and dried at 60°C in a vacuum oven. Polymerization runs using only the ammonium persulfate gave polymer of excessive molecular weight which was only swollen by acetone or DMF as shown in Table 6. Decreasing the redox catalyst concentration to half the previous amount (Run 94-6) gave polymer of higher intrinsic viscosity which formed stronger polymer films than those formed from polymer of lower intrinsic viscosity (Run 18). Polymer of 1.6 intrinsic viscosity was used in the evaluation of this new material.

EVALUATION

Poly(diacetone acrylamide) was evaluated in the form of dried films prepared by casting a 20% solution in DMF and allowing it to dry overnight at 65°C. The films were stripped from the glass plates after a thorough soaking in distilled water. The salt permeability, diffusion constant, and distribution coefficient of these films were determined by the electrical conductivity method.[9] These data are presented in Table 7. Both films sorbed water to

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* The Lubrizol Corporation, Plastic Chemicals Department, P.O. Box 3057, Cleveland, Ohio, 44117.

TABLE 6

POLYMERIZATION OF DIACETONE ACRYLAMIDE

Run No.[a]	DAA, g	H_2O, g	$(NH_4)_2S_2O_8$, g	$NaHSO_3$, g	Temp., °C	Visc., [η][b]	Polymer Solubility
18	50	400	0.66	0.34	22	0.74[c]	Sol. acetone, DMF
26	100	800	1.32	0.0	21	-	Insol. acetone, DMF
31	100	800	3.3	0.0	40	-	Insol. acetone, DMF
94-6	100	800	0.66	0.34	22-25	1.6[d]	Sol. acetone, DMF

[a] All runs gave 95% yield or more.

[b] Intrinsic viscosity.

[c] In acetone solution, 25°C.

[d] In DMF solution, 30°C.

TABLE 7

SALT PERMEABILITY AND DISTRIBUTION COEFFICIENT
OF POLY(DIACETONE ACRYLAMIDE)

Film[a]		D_2K,[b]	D_2,[c]	
Thickness, mils	H_2O, %	cm^2/sec	cm^2/sec	K[d]
2.2	14.9	2.93×10^{-12}	1.12×10^{-10}	0.026
1.1	15.2	2.27×10^{-12}	7.90×10^{-11}	0.029
e	13-15	2×10^{-11}	6×10^{-10}	0.03

[a] Film prepared by casting from 20% polymer in DMF solution. Drying at 65°C overnight and removal from plate in distilled water.

[b] Sodium chloride permeability.

[c] Sodium chloride diffusion constant.

[d] Sodium chloride distribution coefficient.

[e] Typical values for cellulose acetate, E 398-3.

the extent of about 15% and were quite elastic. On the other hand, the completely dried films appeared quite brittle, indicating that the polymer is highly plasticized by water. The salt permeability value (D_2K) and salt diffusion constant (D_2) were considerably lower than values obtained for cellulose acetate.[9] The salt distribution coefficient, K, was about the same as that of cellulose acetate.

Films of 0.65 and 0.80 mils thickness developed pinholes during testing at 1500 psi with 3.5% sodium chloride solution and it was apparent that stiffer and stronger films of the polymer were necessary. Thicker films of poly(diacetone acrylamide) that had been cast for salt-permeability determinations were therefore used for reverse osmosis at 1500 psi with 3.5% sodium chloride feed solution to determine water permeability. The data are presented below.

Film Thickness, mils	Operating Time, hours	Flux, gfd
2.2	1.0	0.0
1.1	16.2	0.0062

The 2.2-mil-thick film of poly(diacetone acrylamide) allowed no detectable flow of product water and was obviously too thick. The 1.1-mil film gave a measurable but very low flux (0.0062 gfd). No salt-retention values were determined, because insufficient sample was obtained to permit testing. The 1.1-mil film was run on a 1000-Å Millipore support that was in turn supported by No. 50 Whatman filter paper on the porous stainless steel plate.[8]

Although the salt permeability of poly(diacetone acrylamide) film is lower than that of cellulose acetate, the water-permeability value appears to be very much lower. The unusually low water permeation may also be related to the mechanical properties of the film. The highly water-plasticized film of poly(diacetone acrylamide), which is very extendable and plastic, could have extruded into the pores of the support material at 1500 psi and greatly increased the effective thickness, thus reducing the water flux.

The tensile properties of the poly(diacetone acrylamide) film were determined for comparison with those of cellulose acetate. Poly(diacetone acrylamide) having an intrinsic viscosity of 1.6 in DMF solution at 30°C was cast in a 10-mil wet thickness from a 22% solution in acetone and was allowed to air-dry. The film was further dried overnight in a convection oven at 65°C and was removed from the glass plate by soaking in deionized water. Tensile specimens 0.506 cm wide were cut from the 1.35-mil-thick film. Tensile tests run in water at 25°C showed that the film elongated about 23% (to the limit of the test fixture) without reaching the break point. The modulus was too low to be determined. The maximum stress reached at 23% elongation was only 7 kg/cm^2, which is very low compared with maximum stresses of 207 kg/cm^2 for cellulose acetate film. With the very low modulus and great plasticity of poly(diacetone acrylamide), the film could very well have extruded into the

pores of the Millipore support material, thus increasing the effective thickness and decreasing the apparent flux. Because of the apparent low flux of this polymer, further work was not conducted with films of poly(diacetone acrylamide). Its plastic nature and low salt permeability (D_2K), however, suggested its use as an external plasticizer for vinylene carbonate polymers.

EXTERNAL PLASTICIZERS FOR POLY(VINYLENE CARBONATE)

The external plasticization of poly(vinylene carbonate), by blending with compatible polymers, was investigated in an effort to prepare a more plastic film that would retain the excellent osmotic properties of poly(vinylene carbonate). The polymers chosen to blend into poly(vinylene carbonate) should be plastic and, ideally, should have good osmotic properties to contribute to the polyblended film.

POLY(DIACETONE ACRYLAMIDE) BLENDS

Since poly(diacetone acrylamide) (PDAA) proved to be highly plasticized with water and exhibited a low salt permeability, it was chosen for initial study in attempts to externally plasticize poly(vinylene carbonate). The polymer blend proportions and osmotic properties of films made from the blends are presented in Table 8. Initially, the osmotic properties of the film from blend No. 1 (14.7% PDAA) appeared very promising (a calculated flux of 8.3 gfd at 2500-Å thickness with 93.4% retention), but the flux increased and salt retention decreased with time. Less PDAA was incorporated into blend No. 2 and the solvent for the casting solution was made with 33.3% DMSO based on the acetone in an attempt to increase the percent polymer in the casting solution. This film had a higher flux and a slightly lower salt retention than the previous film prepared from acetone solution. The amount of PDAA was further reduced in blend No. 3 because of the high flux exhibited in blend No. 2, and the solvent was based on pure DMSO to enable more polymer to be formulated into the casting solution. This film had a lower flux than that for blend No. 2 initially, but the flux increased significantly over 22.6 hours operating time and the salt retention again fell off to a value of 57.8%.

The foregoing blend films of poly(vinylene carbonate) and PDAA exhibited unusually high flux values. These high flux values could be caused by the added PDAA, the DMSO solvent, which is quite difficult to remove completely from dried films before immersion in water, or from the unusually high humidity at the time of film casting. To investigate these high values, a film was prepared without using external plasticizer, and under very-low-humidity conditions. Film No. 4 was cast from poly(vinylene carbonate)-DMSO solution in a dry box, was transferred to a convection oven at 62°C, and was allowed to dry with the oven blower off to ensure even drying. The film was further dried overnight with the blower on at 62°C. The film was then kept under vacuum for 8 hours in an attempt to remove all of the high-boiling-point DMSO solvent before immersion of the film in water. The reverse-osmosis properties of this film indicated a high water flux which increased with time. In general, the salt retention also improved with time, giving a final retention of 92.2% at a flux of 2.82 after 22.4 hours. It is probable that if

TABLE 8

POLY(VINYLENE CARBONATE) POLYMER BLENDS

Polymer Blend No.	Wt% PDAA[a] Blended with PV Carbonate	Solvent Type	Solvent %	Film Casting	Film Thickness mils	Oper. hours	Flux[b] gfd	Calc. Flux for 2500 Å gfd	Salt Ret. %
1	14.7	Acetone	94.3	Canopy[c]	0.20	3.7	0.41	8.3	93.4
						22.6	3.05	61.9	42.1
2	7.5	2 Acet, 1 DMSO[d]	90.0		0.30	5.1	0.81	30.5	86.3
3	4.1	DMSO	88.9		0.20	2.9	0.80	16.2	84.2
						5.4	0.79	16.0	91.2
						22.6	2.69	54.6	60.0
						28.3	2.33	47.4	57.8
4	0.0	DMSO	89.2	Dry box, oven, vac. at 60°C	0.20	2.1	1.17	23.8	89.7
						5.3	1.05	21.3	88.5
						21.7	2.60	52.8	93.1
						22.4	2.82	57.2	92.2
5	9.1[e]	DMSO	90.0	Dry box, oven at 60°C	0.30	2.1	0.60	19.8	57.5
						19.7	0.90	29.7	83.1
						24.7	1.31	43.2	83.9
						42.6	1.93	63.7	62.0

[a] Percent poly(diacetone acrylamide) (intrinsic viscosity = 0.76 in acetone at 25°C) based on the poly(vinylene carbonate) of 256,000 mol wt.

[b] Test conditions, 1500 psi, 3.5% sodium chloride.

[c] Plexiglas dust cover to diminish air currents.

[d] Dimethylsulfoxide solvent.

[e] Vithane 100 (Goodyear's polyurethane) used instead of PDAA.

the test had been continued, this film would have eventually exhibited a decrease in salt retention, since the flux had become unusually high, and since the final recorded salt retention showed a slight decrease. It is possible that the air-dried films contained a trace of solvent which was removed during the vacuum storage, leaving extremely small pores which contributed to the unusually high flux.

A comparison of the blended and unblended films indicated that poly(diacetone acrylamide) did not improve the reverse-osmosis properties of poly(vinylene carbonate) in blends up to 14.7%.

VITHANE 100 BLENDS

Vithane 100* was evaluated as an external plasticizer for poly(vinylene carbonate) because of its elastic nature and its apparent compatibility with the host polymer. Vithane 100 is a new, partially crosslinked polyurethane resin of high molecular weight that is soluble in DMSO and yields films with high tensile strength and elongations up to 850%. A blend of 9.1% Vithane 100 and 90.9% poly(vinylene carbonate) in DMSO was used to prepare films. These films (Table 8) showed increasing fluxes and eventual decreasing salt retentions with time, indicating that the added Vithane 100 adversely affected the reverse-osmosis properties of the blend film.

TENSILE PROPERTIES OF BLENDS

The tensile properties of poly(vinylene carbonate) polyblend films were determined and compared with the tensile properties of the poly(vinylene carbonate) homopolymer film to determine whether the added polymers exhibited a plasticizing effect. The tensile properties were determined on film under water at a crosshead speed of 0.05 in. per min. The data are summarized in Table 9. The tensile property data show that 7.7% of added PDAA acted as a very weak external plasticizer, reducing the stiffness, yield point, and tensile strength of poly(vinylene carbonate) and slightly increasing the elongation at break. Vithane 100 at 9.1% concentration made the poly(vinylene carbonate) blend film somewhat stiffer, with a slightly lower yield and break point. The elongation at break, however, was about the same. This indicated that Vithane 100 did not act as an external plasticizer for poly(vinylene carbonate).

POLYACETOXYMETHYLENE

The program of investigation of poly(vinylene carbonate) and its derivatives included an evaluation of polyacetoxymethylene. This derivative offers greater solubility than the parent polymer in acetone and other common solvents and thus a better opportunity for membrane fabrication by the techniques proven successful with cellulose acetate. Therefore, the preparation and evaluation of polyacetoxymethylene was undertaken.

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* The Goodyear Tire and Rubber Company, Akron, Ohio.

TABLE 9

MECHANICAL PROPERTIES OF POLY(VINYLENE CARBONATE) POLYBLENDS

	Elastic Modulus $kg/cm^2 \times 10^{-3}$	Yield kg/cm^2	Break kg/cm^2	Elongation, % Yield	Break
Poly(vinylene carbonate)	29.6	300	301	1.29	1.41
Poly(vinylene carbonate) (7.7% PDAA)[b]	22.4	208	208	1.22	1.45
Poly(vinylene carbonate) (9.1% Vithane 100)[c]	34.7	283	284	0.97	1.40

[a]Tensile properties determined on film under water at a crosshead speed of 0.05 in. per min.

[b]Poly(diacetone acrylamide) (intrinsic viscosity = 0.76 in acetone at 25°C).

[c]Trade name of Goodyear crosslinked polyurethane polymer.

Polyacetoxymethylene was prepared according to the procedure of Field and Schaefgen[10] by the esterification of polyhydroxymethylene with acetic anhydride in molten urea, but in batch sizes about 100 times greater than employed by these authors. In the first step, polyhydroxymethylene was prepared by the hydrolysis of 0.3-mil-thick dried films of poly(vinylene carbonate) (250,000 mol wt) cast from acetone solution onto glass plates. The hydrolysis was conducted in a 1% solution of sodium methylate in methanol at 55°C over a 16-hour period. The resulting polyhydroxymethylene film was washed with methanol and then with water followed by drying in a vacuum oven at 60°C. The dried polyhydroxymethylene film (0.3 g) was charged along with 10 g of urea (containing 5% anhydrous sodium acetate) to a small three-necked flask equipped with a stirrer, a closed addition funnel, and a distillation head. The flash was heated with stirring in an oil bath at 140°C while a stream of nitrogen was passed through the flask to remove oxygen. The addition of nitrogen was stopped when the contents reached the temperature of the bath. A drying tube was then substituted for the gas inlet, and acetic anhydride was added from the dropping funnel with stirring. A clear solution resulted after addition of the acetic anhydride. The oil-bath temperature was raised to 160°C and by-product acetic acid was distilled away. Without cooling, the reaction mixture was poured into distilled water to precipitate the polyacetoxymethylene. After warming the resulting mixture to 70°C to dissolve the by-product N-acetylurea, the polymer was collected by filtration, washed with water, and dried. The light tan polymer, obtained in 66% yield, had a specific viscosity (0.08% in acetone solution) of 0.32 at 25°C. The parent polymer, poly(vinylene carbonate) of average molecular weight 250,000, had a specific viscosity of 0.98 in acetone at the same concentration.

Dried films, 8.9-μ-thick, prepared from a 13% solution of polyacetoxymethylene in acetone, were clear but weak and brittle. The infrared spectrogram of the dried polyacetoxymethylene film, presented in Figure 5, agrees well with the curve obtained by Field and Schaefgen[10] for their polymer. The band at 5.5 μ is considered by Field and Schaefgen to be a combination band not related to the presence of carbonyl.

The above work was repeated using poly(vinylene carbonate) of higher molecular weight and decreasing the time of acetylation in molten urea in an attempt to decrease the apparent degradation of the polymer. Poly(vinylene carbonate) of 485,000 molecular weight was hydrolyzed in 1% sodium methylate in methanol as before. The polyhydroxymethylene obtained was then acetylated under the same conditions used previously except that the acetylation time in molten urea was reduced from 1 to 0.5 hour. The product was worked-up as before. Clear films, 20.8-μ-thick, cast from acetone solution, again were weak and brittle and not suitable for use as films or membranes. The specific viscosity (0.08% in acetone solution) was only 0.25 compared with 1.36 for the parent polymer. This indicates that extensive polymer degradation had again occurred and appears to be independent of a change in the conditions of acetylation in molten urea. On the basis of these results, it was concluded that polyacetoxymethylene prepared in this manner is not suitable for membrane use and the work was discontinued.

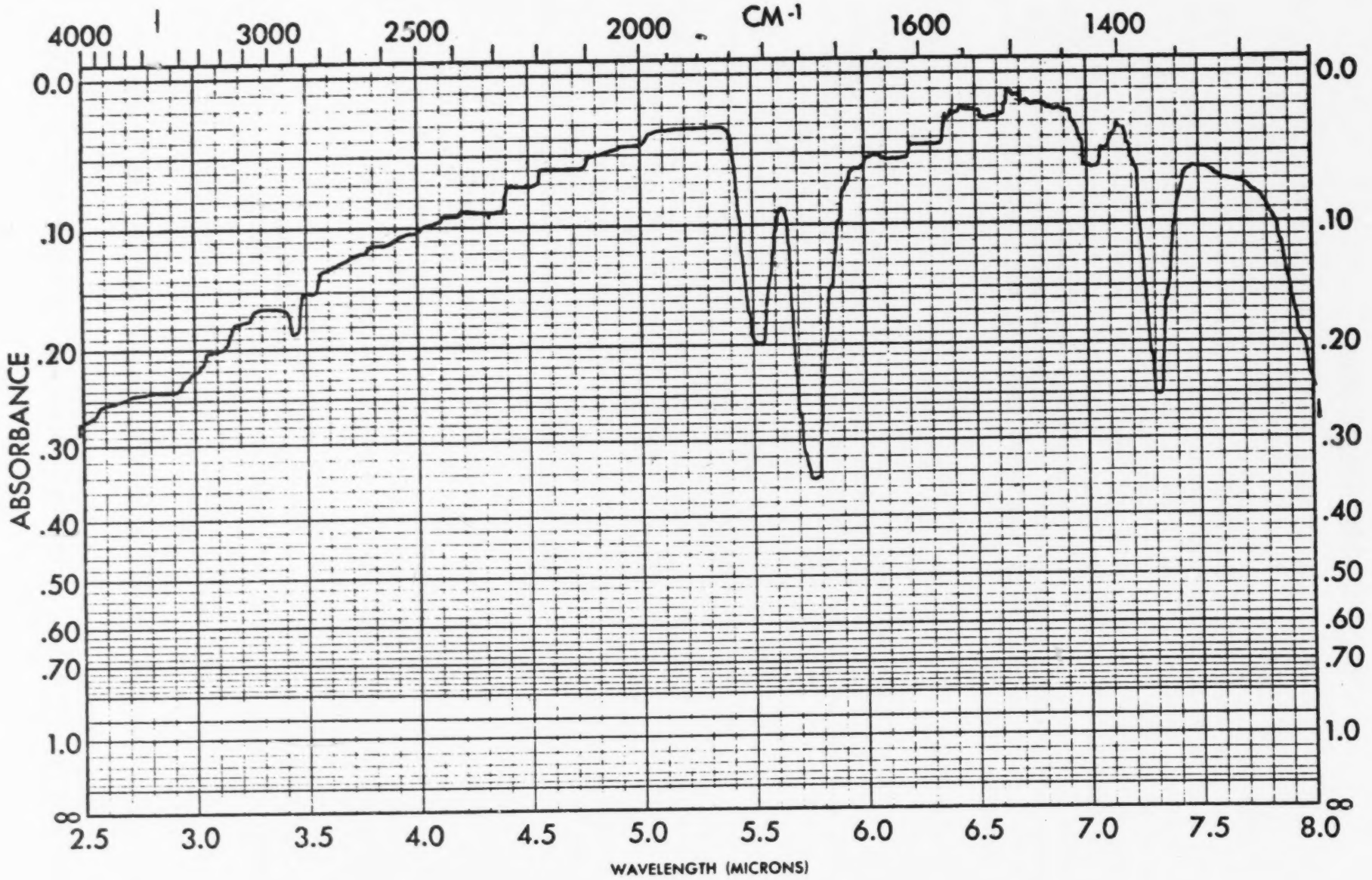


Figure 5

INFRARED SPECTROGRAM OF A POLYACETOXYMETHYLENE FILM

METHACRYLONITRILE POLYMERS

Polymers and copolymers prepared from methacrylonitrile were investigated in an effort to capitalize on the highly polar nitrile group and the outstanding strength and stability of nitrile polymers. In a previous investigation,[2] polyacrylonitrile had been found difficult to fabricate into membranes because it is soluble only in high boiling solvents. Polymethacrylonitrile is acetone soluble but previous evaluation[2] of films of the polymer indicated that its salt retention is in the order of 10%. It thus appeared that polymethacrylonitrile required chemical modification to improve its osmotic characteristics. Therefore, chemical modification, including hydrolysis of the homopolymer and the preparation of copolymers to introduce other polar groups, was undertaken. First, however, the mechanical properties of the methacrylonitrile homopolymer required evaluation to determine if membranes based on the modified polymers might have adequate strength.

MECHANICAL PROPERTIES

Polymethacrylonitrile was prepared from the monomer by emulsion polymerization. Methacrylonitrile* was purified by washing three times in a separatory funnel with 1% aqueous sodium hydroxide solution, followed by water washing and drying over anhydrous calcium chloride. The dried monomer was charged to a spinning band column and distilled at a 5/1 reflux ratio. Distilled water (60 cc) and potassium persulfate (0.15 g) were charged to a 200-ml polymer flask and nitrogen gas was bubbled through the solution to remove air. Detergent** (0.15 g) was then added followed by further nitrogen gas purging. Freshly distilled methacrylonitrile (24 cc) was added to the catalyst solution and the mixture was shaken and cooled to Dry Ice temperature under a slight vacuum and sealed off at full pump vacuum. Next, the flask was transferred to a water bath at 50°C, and was tumbled for 24 hours. The water bath temperature was then increased to 80°C and the flask was tumbled for 16 hours. After removing the flask from the bath, it was cooled and opened. The emulsion was broken by adding 50 g of sodium chloride with stirring; the polymer was filtered off and washed three times with 5% aqueous sodium chloride solution, followed by water washing. The polymer was dried and dissolved in acetone, filtered, and reprecipitated in water, yielding a fine precipitate with a specific viscosity of 1.62 (0.063 g/100 cc in acetone at 25°C). Films were cast from a 10% polymer solution in acetone for evaluation of the tensile and reverse-osmosis properties. The wet tensile properties*** of this film are given below:

Elastic Modulus $kg/cm^2 \times 10^{-3}$	Yield kg/cm^2	Break kg/cm^2	Elongation, % Yield	Break
30.3	220.3	220.9	0.90	2.29

* Eastman Organic Chemicals Distillation Products Industries, Rochester, N.Y. (White Label).

** DuPont's Duponol ME Dry Surface Active Agent.

*** Film thickness was 1.95 mil; crosshead speed was 0.05 in./min.

The stiffness, tensile strength, and plasticity of the polymer appeared to be adequate; this suggested that copolymers based primarily on methacrylonitrile would be strong enough to be useful as reverse-osmosis membranes.

COPOLYMERIZATION STUDIES

The preparation of methacrylonitrile-acrylamide and methacrylonitrile-vinylpyrrolidone copolymers was carried out in a manner similar to that used for the preparation of the homopolymer. The caustic-washed and dried methacrylonitrile monomer was distilled through a spinning-band column at a 10/1 reflux ratio. The acrylamide was used without further purification. The N-vinyl-2-pyrrolidone was also distilled through a spinning-band column at a 10/1 reflux ratio; a middle cut was taken for use. The comonomer and catalyst ratios, and an analysis of the polymer are shown below, along with data on the methacrylonitrile homopolymer.

Polymer No.	Comonomer, g			H_2O[a] g	Spec. Visc.[e]	$K_2S_2O_8$ Cat., g	Analysis		
	MAN[b]	AA[c]	VP[d]				C	H	N
31	19.2	1.0	-	60	2.62[f]	0.15	70.62	7.24	20.46
35	19.2	-	3.1	60	1.72	0.15	69.9	6.38	20.20
43	19.2	7.0	-	90	-	0.25	69.63	7.82	20.35
25	19.2	-	-	60	1.62	0.15	70.73	7.76	20.43

[a] The distilled water contained 0.15 g of Duponol ME detergent.

[b] Methacrylonitrile.*

[c] Acrylamide.**

[d] N-vinyl-2-pyrrolidone.**

[e] Specific viscosity (0.063 g polymer per 100 ml acetone at 25°C).

[f] Viscosity of acetone soluble fraction. Acetone insol fraction gave 4.97 viscosity in DMSO solution.

The copolymer preparations were worked up in a manner similar to that of the methacrylonitrile homopolymer. Polymer 31, the methacrylonitrile-acrylamide copolymer, was only partially soluble in acetone. The acetone insoluble portion was soluble in DMSO and appeared to be different only in molecular weight. Polymer 43 was prepared in an attempt to incorporate a substantial amount of acrylamide comonomer.

From the nitrogen analysis of the copolymers and PMAN homopolymer, the calculated amount of acrylamide incorporated into the MAN-AA copolymer was essentially none for Polymer 31, which was prepared with 5% of acrylamide comonomer, and 1% for Polymer 43 using 27% acrylamide. The calculated amount

* Eastman Organic Chemicals, Distillation Products Industries, Rochester, N.Y. (White Label).

** Monomer-Polymer Laboratories, The Bordon Chemical Co., Philadelphia, Penna.

of vinylpyrrolidone incorporated into the MAN-VP copolymer was 4%. The main problem with the aqueous copolymerization appears to be the difference in the solubility of the methacrylonitrile and the acrylamide, or vinylpyrrolidone comonomer, both of which are completely soluble in water, whereas the methacrylonitrile is soluble to the extent of only 2.8% at 60°C. Possibly the comonomers substantially homopolymerized in the reaction mixture and the water soluble polyacrylamide or polyvinylpyrrolidone in each case was washed out during polymer work-up. The emulsion copolymerization may require better agitation than the approximately one-revolution-per-sec tumbling action used in the water bath. However, the reaction mixture had the appearance of a good emulsion.

The salt retention properties of the copolymer films were approximately that of the homopolymer, as shown below:

Polymer No.	Type	Film Thick., mils	gfd	2500 Å Calc. Flux, gfd	Salt Retention, %
31	MAN/AA	0.30	0.41-0.33	10-12.5	7-15
35	MAN/VP	0.40	0.61-0.63	24.8-25.8	6-10
25	MAN	0.35	1.4 -3.0	50-104	8-12

Although there are undoubtedly other procedures to encourage the copolymerization of MAN with acrylamide and vinylpyrrolidone, the low desalination results did not warrant further expenditure of effort in this direction. Therefore, emphasis was shifted toward the hydrolysis of polymethacrylonitrile to enhance its osmotic properties.

HYDROLYZED POLYMETHACRYLONITRILE

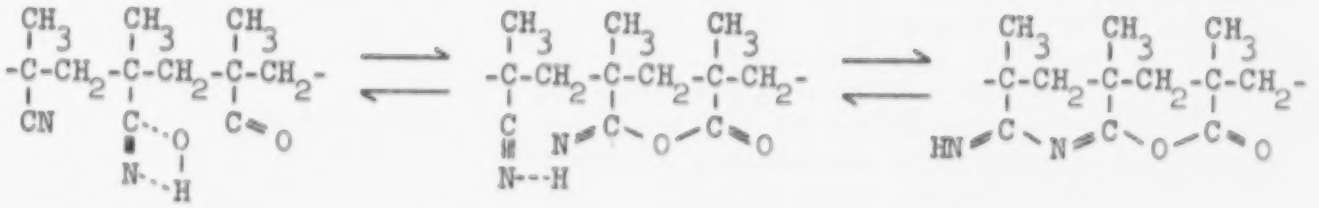
The introduction of amide or carboxyl groups in place of some of the nitrile groups in the polymethacrylonitrile polymer would be expected to increase the water sorption properties of the polymer and thus improve the osmotic properties of the polymer. The acid hydrolysis of polymethacrylonitrile to introduce carboxyl groups was therefore investigated.

The hydrolysis of polymethacrylonitrile was conducted in concentrated hydrochloric acid solution. The polymer, 2 g, was dissolved in 250 cc of C.P. concentrated hydrochloric acid by rolling in a bottle overnight. The clear solution was poured into 3 liters of rapidly stirred, deionized water. A white, stringy polymer was obtained. The polymer was collected on a filter, washed once, and blended in a Waring Blender with distilled water. After repeating the washing procedure in the Blender, the polymer was extracted with hot water in a Soxhlet apparatus for 16 hours. The hot water extracted about 10% from the original charge. The residue was not soluble in acetone in contrast to the ready solubility of the parent polymethacrylonitrile. The hydrolyzed polymer was soluble both in DMSO and in anhydrous formic acid. A 7.5% solution of the hydrolyzed polymer in DMSO solution was quite viscous.

A film cast from DMSO solution and hot-air dried absorbed 15.8% water. An acid number of 0.627 meq/g, corresponding to 4.2% carboxyl groups, was found for the polymer.

Reverse-osmosis tests on a 0.40-mil dried film cast from DMSO solution gave from 27 to 38% salt retention, with fluxes in the range from 0.04 to 0.06 gfd_o (equivalent to a calculated flux of about 2 gfd at a film thickness of 2500 Å).

In the above hydrolysis, the hydrochloric acid solution of polymethacrylonitrile was poured into rapidly stirred water to complete the hydrolysis. In order to increase the extent of hydrolysis, water was added slowly to the rapidly stirred acidic polymer solution (the reverse of the above technique). This procedure allowed the water, acid and polymer to interact over a longer time period. Polymethacrylonitrile, 4.0 g, was added to 250 ml of concentrated CP hydrochloric acid in a glass bottle which was then rolled until all the polymer dissolved. The clear solution was transferred to a beaker and stirred rapidly while 3.5 liters of distilled water was added slowly to precipitate the polymer. The product was washed with water three times on a filter, transferred to a Waring Blender and blended with distilled water followed by a final filtration. The polymer was then dried, charged to an extractor and extracted with hot water. During the initial stages of the extraction, the polymer turned a bright yellow but the color disappeared during the final period of extraction. The yellow color indicates the presence of conjugated unsaturation believed to be similar to that reported by N. Grassie.[11] The reaction leading to a conjugated structure is initiated between adjacent nitrile and carboxyl groups resulting in a proton migration and ring closure. The imine group formed reacts with an adjacent nitrile group by means of a proton shift and the reaction continues down the chain through nitrile groups resulting in the formation of the conjugated structure shown below:



The conjugated structure is reported to be stable only at the higher temperatures. Other non-conjugated interactions between carboxyl and adjacent nitrile groups, however, may be stable at ambient temperatures. The material removed from the polymer by hot-water leaching amounted to 7.5% by weight of the original charge. The water insoluble portion had an acid number of 0.886 meq/g corresponding to 9.5% carboxyl groups. The introduction of carboxyl groups was approximately doubled by the modified hydrolysis procedure, but this increase was not considered enough to make an appreciable difference in the osmotic properties of the material. In addition, the possibility that the carboxyl groups may be strongly associated with adjacent nitrile groups is a complicating factor and efforts were made to obviate this interaction by eliminating the hot-water treatment.

A second portion of the same polymethacrylonitrile was dissolved in concentrated hydrochloric acid and precipitated as above by adding water to the acid solution. The polymer was not hot-water extracted, but was merely washed and dried. An acid number of only 0.29 meq/g equivalent to 3.1% carboxyl groups was obtained. A 0.35-mil-thick film of this polymer was prepared from a 10% solution of the polymer in acetone. The results summarized below show little difference in salt retention between the membranes prepared from either polymer.

		Reverse Osmosis Properties at 1500 psi	
Polymer Type	% COOH	Calc. Flux for 2500 Å Film	Salt Retention, %
Hydrolyzed PMAN + Hot H_2O Extraction	9.5	2.0	27-38
Hydrolyzed PMAN	3.1	14.9	23

Because of the low salt retention of the hydrolyzed polymethacrylonitrile film and the problems encountered in the interaction of adjacent groups, no further work was conducted on this material.

MELAMINE RESINS

A brief study of the applicability of melamine resins for the preparation of desalination membranes was undertaken. The basis for this study was the observation, during a reverse-osmosis pilot plant run, that insertion of a melamine impregnated filter in the feed-water line reproducibly caused a temporary drop in salt permeation of the unit. No such effect was noted with phenolic impregnated filters. An investigation indicated that material was being leached out of the filter by the feed water and was increasing the salt retention of the membranes in the unit. Hot-water extraction of the filter material resulted in removal of a water soluble, low molecular weight melamine-formaldehyde resin amounting to 7% of the filter weight. It seemed appropriate, therefore, to determine whether melamine-formaldehyde resins exhibit properties applicable to the preparation of desalination membranes.

Liquid, castable melamine-formaldehyde oligomers can be prepared by the reaction of melamine and formaldehyde in different ratios and allowing the condensation reaction to proceed by the removal of product water. Attempts were also made to prepare the liquid oligomers from hexamethylolmelamine by heating it near its melting point and allowing condensation reactions to proceed. It was anticipated that the liquid oligomers, cast in the form of wet films, could then be allowed to partially dry and cure or condense further before gelation.

PREPARATION AND EVALUATION OF HEXAMETHYLOLMELAMINE

Hexamethylolmelamine was prepared in 40% yield by reacting formaldehyde with melamine under alkaline conditions. The experimental procedure was as follows. To a 500 ml 3-necked flask equipped with a stirrer and a

condenser and supported on a steam bath were added 37.8 g of melamine and 195 g of 37% aqueous formaldehyde solution made slightly basic (pH 7.5) with dilute sodium hydroxide solution. The mixture was stirred and heated on a steam bath until the melamine dissolved and formed a clear solution. The solution was heated 10 min more at steam bath temperature and then cooled. The cooled solution solidified and the crystals were washed 4 times with reagent grade isopropanol. The product, m.p. 138-142°C, was first dried in air then under vacuum at 50°C to remove isopropanol. Attempts were made to form liquid oligomers from the hexamethylolmelamine by heating to a temperature above the melting point of the compound. The molten material, however, quickly resolidified at temperatures in excess of the melting point, presumably due to further reaction to form a solid condensation product.

Emphasis was shifted to oligomers prepared from the reaction of melamine and formaldehyde by varying the ratio of the reactants and the extent of condensation reaction.

LIQUID MELAMINE-FORMALDEHYDE CASTING RESINS AND PREPARED FILMS

A study of the reaction of melamine with formaldehyde to produce liquid prepolymers suitable for film casting was conducted. The optimum mole ratio of 37% formaldehyde to melamine for the preparation of a liquid, castable resin was found to be 4.5:1. The 37% formaldehyde solution was neutralized with 1.0 molar sodium hydroxide solution to a pH of 7.0 before use. The reactants were heated to reflux temperature on a steam bath and stirred for 0.5 hours. An amount of water corresponding to 30% of the total weight of the reaction mixture was then removed under vacuum (water aspirator). The resultant clear resin had approximately the same viscosity as cellulose acetate casting dope. The pot life of the resin was unpredictable (2 hours to 3 days) and depended on the amount of water removed and the reaction temperature during water removal.

When cast into a film, the liquid resin formed a skin very readily on partial drying but required thermal curing to produce an unsupported film. Curing at temperatures less than 105°C for 2 hours resulted in a film which was sticky and weak after water immersion. Longer times of higher temperatures produced hard and glossy films. A film cured at 105°C for 2 hours was quite pliable when wet but became brittle when dry.

The melamine-formaldehyde films adhered strongly to glass and most other surfaces tested. Partial release from silicone-coated paper taped to glass was achieved with a film containing 20% glycerine. All the films had defects and, as a result, 3-in. circles were not obtained for reverse-osmosis testing. A salt permeability value ($D_2K = 5.70 \times 10^{-9}$ cm^2/sec) was determined on a 1-in. diameter circle of film which appeared defect-free. A value for water permeability would be required in addition to D_2K in order to estimate the salt retention capability of the material. However, because of the short pot life of the resin, the narrow curing range of the cast film and its adhesive nature, no further work was conducted with this material.

COLLAGEN FILMS

GENERAL CONSIDERATIONS

The investigation of collagen films of a high degree of crystallinity for possible reverse-osmosis use was undertaken because of several favorable considerations. First, recent development of a microcrystalline form of collagen* by Dr. O. A. Battista[12] of FMC Corporation has enabled the preparation of stable, colloidal dispersions of collagen. In concentrations near 1%, the dispersions approach the viscosity of cellulose acetate casting solutions and films of sufficient thickness can be cast to yield on drying transparent and strong collagen films. Second and perhaps more important, is that the colloidal dispersion of collagen may be deposited on solvent filled, porous support surfaces (e.g., Metricel filters) in the form of a continuous thin film. The adhesive nature of collagen would obviate the need to bond the film to the support. Finally, collagen contains the highly polar carbonyl-, amino-, hydroxyl- and carboxyl groups which should aid in high water transport properties. Films of collagen are swollen by water and may be readily crosslinked through the polar groups to control the degree of swelling and the strength of the film.

The principal amino acids comprising the protein polymer, collagen, are glycine, proline, hydroxyproline, alanine and glutamic acid, which represent about 63% of the polymer. The other naturally-occurring amino acids with the exception of cystine and tryptophane make up the remainder.

The absorption of water by collagen is rapid and is dependent on the vapor pressure of water in the atmosphere. Part of the absorbed water is in the form of water of hydration (bound water) and constitutes about 20% of the weight of the polymer.[13] The bound water is thought to be associated with either the polar side chains or the peptide bond.

Collagen is somewhat analogous to cellulose in its solubility behavior and its ability to be regenerated from special solutions. Thin films of collagens have also been prepared by the spreading of monolayers of solubilized collagen solutions on the surface of liquids.[14] Effective crosslinking of collagen films is considered necessary to prevent any possible detrimental lyotropic effects of neutral salts such as magnesium or calcium chloride. These salts tend to weaken the secondary valence forces of hydrogen bonding, electrostatic crosslinking and Van der Waals forces.[15] Strong primary crosslinking forces would be expected to overcome any of these lyotropic effects and result in stabilized collagen films. Films from microcrystalline collagen can be crosslinked with formaldehyde, glutaraldehyde, alum and other suitable chemical crosslinking agents.[16] Hexamethoxymethylmelamine is a water soluble crosslinking agent and can be added to the colloidal collagen casting solution. Physical means for crosslinking collagen films include ultraviolet irradiation and heat (110° - 150°C).

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* Avitene-H, FMC Corporation, Central Research Department, Box 8, Princeton, N.J., 08540.

COLLAGEN CASTING DISPERSIONS

Colloidal casting dispersions of microcrystalline collagen ranging in concentrations from 0.25 to 1.0% were prepared for initial film evaluation and are presented in Table 10. The dispersion medium and collagen were charged to a Waring Blender, allowed to soak for 5 min, blended for 5 min at a transformer setting of 35 volts followed by 10-15 min at a setting of 90 volts. The resulting dispersions were filtered through a 70 x 100 fiber-count/in. nylon parchment into a bottle.

Useful casting dispersions in distilled water were made with microcrystalline collagen concentrations in the range of 0.25 to 0.50%. Beyond 0.50% collagen concentration, the casting dispersions tended to gel and could not be cast. Using equal parts of an organic solvent with water, however, allowed concentrations of collagen to be approximately doubled. Mixtures of water with 50% methanol, ethanol, isopropanol or acetone in each case were used to make colloidal casting dispersions of collagen in the concentration range of from 0.5 to 1.0%. A 50/50 (w/w) water/methanol solution containing a collagen concentration of 0.64% had a viscosity somewhat greater than that of a 20% cellulose acetate casting solution. From this casting formula, wet films of 100 mils thickness could easily be cast.

CASTING, CROSSLINKING AND EVALUATION OF COLLAGEN FILMS

The adhesive nature of collagen films required a careful selection of casting surfaces in order to permit the release of the dried films (Table 10). Collagen films cast on glass or aluminum-coated Mylar could not be removed because of extreme adhesion. Films cast on clear polyethylene, uncoated Mylar or Teflon sheet could only be removed in small sections with difficulty. Wet films cast on a paraffin-wax-coated glass surface crawled extensively. The best surface for casting was found to be a wax-extended polyethylene sheeting taped to glass. The castings did not crawl on this surface and the films were quite easily removed by stripping them from the sheet after drying. Films with dry thicknesses less than 0.5 mil were found to be more difficult to handle and remove from the casting surface than thicker films.

Crosslinking of microcrystalline collagen films by thermal and ultraviolet treatment was investigated. The effectiveness of the treatment in crosslinking the collagen was assessed by determination of the swelling ratios in water before and after treatment. Irradiation of a dry collagen film at a distance of 10 in. from a 140 watt ultraviolet mercury lamp (Hanovia N251) for 1 hour at 39°C gave no change in swelling (thickness) ratio over the untreated material (4.95:1 - wet thickness:dry thickness). Heating collagen films to 150°C for 6 hours gave a reduction in swelling ratio to 2.75:1. Heat treatment of a collagen film containing hexamethoxymethylmelamine (8% based on collagen) at 150°C for 6 hours gave the lowest swelling ratio (1.27:1). The best crosslinking agent for dry collagen films thus appears to be hexamethoxymethylmelamine at temperatures of 150°C. Heating alone at 150°C affords a moderate amount of crosslinking to render the film non-redispersible in water.

TABLE 10

COLLAGEN FILMS FROM COLLOIDAL CASTING DISPERSIONS

	Casting Dispersion						Collagen Film				
		Solvent									
Film No.	Collagen[a] %	H_2O, %	Organic Type	Organic %	Cymel[b] %	Viscosity	Wet Thick., mils	Casting Surface	Wet Film Properties	Dry Temp., °C	Dry Film Adhesive Properties
1	0.25	99.75	-	-	-	low	20	Glass	smooth	25	adhered
2	1.0	49.5	2-propanol	49.5	-	high	40	↓	↓	40	↓
3	0.25	99.75	-	-	-	low	50	Clear PE film	↓	42	↓
4	1.0	49.5	2-propanol	49.5	-	high	40	↓	crawled	65	off, hard[c]
5	↓	↓	↓	↓	-	↓	40	Al-ctd Mylar	smooth	78	adhered
6	0.5	99.5	-	↓	-	↓	100	↓	↓	78	↓
7	1.0	49.5	2-propanol	49.5	-	↓	40	Unctd Mylar	↓	75	↓
8	0.5	99.5	-	-	-	↓	40	↓	↓	75	off hard
9	0.5	99.5	-	-	-	↓	75	24 mil Teflon	crawled	49	adhered
10	1.0	49.5	2-propanol	49.5	-	↓	100	5 mil Teflon	smooth	82	off hard
11	0.25	99.75	-	-	-	low	50	Wax ctd glass	crawled	46	released
12	1.0	49.5	Ethanol	49.5	-	high	75	Wax-ext'd PE film[d]	smooth	42	released
13	1.0	49.5	2-propanol	49.5	-	↓	75	↓	↓	46	↓
14	1.0	49.48	Ethanol	49.47	0.05	↓	75	↓	↓	35	↓
15	0.64	49.652	MeOH	49.652	0.056	↓	100	↓	↓	54	↓
16	0.64	49.652	MeOH	49.652	0.056	↓	125	↓	↓	45	↓
17	0.5	49.5	Acetone	49.5	-	↓	150	↓	↓	45	↓

[a] Avitene H, FMC Corporation, Central Research Department, Box 8, Princeton, N. J., 08540

[b] Hexamethoxymethylmelamine crosslinking agent, American Cyanamid Company, Plastics and Resins Division, Wallingford, Connecticut.

[c] Film came off surface in pieces with difficulty..

[d] Wax-extended polyethylene film.

Crosslinked collagen films were evaluated for reverse-osmosis performance and the results are presented in Table 11. Film 17, crosslinked by heating to 150°C, had a calculated flux* (274 to 813 gfd) based on a 2500 Å film which was greater than the flux (37.6 to 56.4 gfd) of film 16 crosslinked with the aid of hexamethoxymethylmelamine. Chemical crosslinking was more efficient than simple heating and the greater crosslink density apparently contributed to the much lower flux obtained. The salt retention of the chemically-crosslinked film was greater (43.2 to 47.2%) than that for the thermally crosslinked film (34.8 to 40.6%). The 71C(U) collagen film exposed to ultraviolet irradiation exhibited no change in swelling ratio over that of the untreated film and demonstrated the highest calculated flux range (220 to 1540 gfd) with the lowest salt retention (23.0 to 25.1%). Heat-treating the same film to 150°C for 6 hours reduced the swelling ratio to 2.75:1 and gave reduced calculated fluxes (211 to 657 gfd) and increased desalination (28.2 to 33.9%).

Film 75C was prepared in an attempt to improve the film strength (particularly the tear strength) by the incorporation of polyvinyl alcohol. Polyvinyl alcohol is a good film former and is rendered water insoluble at approximately the same heating temperature used for collagen films. Polyvinyl alcohol,**0.32%, was dissolved in water and 0.45% microcrystalline collagen was dispersed in this medium using a Waring Blender. The colloidal dispersion was filtered through nylon parchment (70 x 100 fiber-count/in.) before casting. Heating the dried film from this dispersion to 145°C yielded a clear film which took on a slightly golden color when rolled up and viewed through several layers. The color may indicate heterogeneity of the film caused by limited compatibility between collagen and polyvinyl alcohol. The film gave calculated fluxes (102 to 254 gfd) somewhat lower than those for pure collagen and probably reflects the lower swelling ratio obtained and the lower water transport properties of polyvinyl alcohol which comprised 41.5% of the solids. The heat-treated collagen-polyvinyl alcohol film did not appear to be stronger or to have better tear-strength than the pure collagen film and therefore further work was not pursued.

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* In addition to the actual fluxes, calculated fluxes for a 2500 Å active-layer thickness are also reported. The calculated fluxes for collagen were initially calculated on the basis of dry film thickness. Subsequently, it was found that collagen films have a high degree of swelling in water; it therefore seemed appropriate to calculate the flux for a 2500 Å thick active layer on the basis of the thickness of the water-swollen film. The true flux value for a 2500 Å thick collagen film will probably lie in between the extreme ranges because of somewhat lower swelling in the saline feed solution used and some compression of the film at the operating pressure. All calculated fluxes for collagen films are therefore reported as a minimum and maximum value on the basis of both dry and wet films, respectively.

** Elvanol, Grade 70-05, polyvinyl alcohol, E. I. duPont de Nemours & Co., Inc., Electrochemical Department, Wilmington, Del.

TABLE 11

REVERSE-OSMOSIS PROPERTIES OF CROSSLINKED COLLAGEN FILMS

Film No.	Casting Dispersion: Collagen[b] %	Solvent: H_2O %	Solvent: Organic Type	Solvent: Organic %	X-Linking Agent: Type	X-Linking Agent: %	Cast Wet Thick., mils	Dry[a] Film Thick., mils	Swelling Ratio in H_2O Wet/Dry	Desalination: 750 psi - 5000 ppm NaCl Solution: Oper. Hours[c]	Flux gfd	Calc. Flux (2500 Å), gfd: Dry	Calc. Flux (2500 Å), gfd: Wet	Salt Ret., %
17	0.52	51.74	Acetone	47.74	Heat	-	150	0.73	2.75/1	0.6	4.0	296	813	40.6
										1.32	3.7	274	753	36.1
										1.73	3.9	288	792	34.8
16	0.64	49.65	Methanol	49.65	Cymel[d]	0.036	100	0.48	1.27/1	1.16	0.77	37.6	47.7	47.2
										3.80	0.91	44.4	56.4	43.2
71C(U)	0.70	49.65	Methanol	49.65	Ultra-violet	-	125	0.65[e]	4.95/1	0.95	4.7	311	1540	23.6
										2.2	4.1	270	1335	23.0
										3.8	4.6	305	1510	25.1
71C(H)	0.70	49.65	Methanol	49.65	Heat	-	125	0.70	2.75/1	0.95	3.3	235	647	33.9
										2.2	2.96	211	580	29.5
										3.8	3.36	239	657	28.2
75C	0.45 0.32 PVA[f]	99.23	-	-	Heat	-	100	0.60	2.1/1	0.95	1.98	121	254	30.8
										2.2	1.67	102	214	26.6
										3.8	1.88	114	239	27.0

[a] Film heated to 150°C for 6 hours to crosslink unless otherwise noted.

[b] FMC Corporation's Avitene-H, microcrystalline collagen.

[c] Films supported on 0.45 μ pore size Metricel Filter supported by No. 50 Whatman filter paper.

[d] Cymel 300 (hexamethoxymethylmelamine), American Cyanamid Company.

[e] Film exposed to a 140 watt Ultraviolet lamp (Canovin R-51) at a distance of 10 in. for 1 hour - maximum temp. 39°C. No further heat-treatment.

[f] Casting dispersion contained pol vinyl alcohol dissolved in the dispersing medium and microcrystalline collagen as the dispersed phase.

In general, the collagen films with the highest swelling ratio gave the highest flux and the lowest percent desalination. Chemical cross-linking using hexamethoxymethylmelamine caused a great reduction in flux and swelling ratio and the highest desalination. The water transport properties of collagen films are high and calculation of the water permeability (D_1C_1) from reverse-osmosis data for film 17 gave values (based on dry and wet thicknesses) of 9.7×10^{-6} and 2.7×10^{-5} g/cm-sec.

DEPOSITION OF COLLAGEN FILMS ON POROUS SUBSTRATES

Most of the colloidal particles in collagen dispersions are less than 1 μ in any dimension. It was thus conceivable that collagen films could be deposited on porous substrates containing an average pore size less than the average particle size of the dispersed colloidal particle. Metricel filter medium of 0.45 μ average pore size was chosen for initial study. A dispersion of 0.25% collagen in distilled water was cast 15 mils wet thickness on a 0.45 μ pore size Metricel filter supported on a glass plate, but the filter was wet unevenly and became wrinkled. A new sheet of Metricel (0.45 μ pore size) was soaked in deionized water and then wiped to remove excess water. A 0.64% collagen 50/50 (w/w) water/methanol casting dope containing 0.056% hexamethoxymethylmelamine crosslinking agent was cast 15 mils-wet-thickness on the wet Metricel and appeared to coat it evenly. Drying of the coated Metricel support in a forced-draft oven at 45°C resulted in a split on one side, possibly as a result of shrinkage of the collagen film. When the coated Metricel filter was removed from the glass plate and then air dried, a definite clear film was observed on the surface of the Metricel. Pieces of the collagen film could be peeled off only with difficulty, indicating that it was bonded reasonably well to the substrate.

The above coating procedure was repeated except that a 50/50 (w/w) water/methanol solution was used to wet the Metricel filter and the casting thickness was set at 20 mils. This collagen-coated Metricel filter did not split on drying at 45°. When the composite was removed from the glass plate by immersion in water, the coating appeared to be uniformly distributed on the Metricel. Drying the coated Metricel at 45°C followed by heating in an oven at 150°C resulted in curling of the film. Immersion of the coated filter in water, however, allowed it to uncurl. This filter (No. 18) gave 16.9 to 17.2% salt retention* (Table 12) with actual fluxes of 19.0 to 19.4 gfd (the thickness of the collagen film was estimated from casting solution concentration and coating thickness to be 2.4 μ). The calculated flux of this film (for 2500 Å) was about 5 times that for the unsupported film cast from the same dispersion (Table 11, Film No. 16). This indicates also that the film deposited on Metricel had imperfections possibly as a result of curling and uncurling.

Collagen casting dispersions (0.64% collagen with 0.056% hexamethoxymethylmelamine crosslinking agent) in a 1:1 water-methanol mixture were also

* Tests conducted at 800 psi - 1.0% sodium chloride feed solution.

TABLE 12

REVERSE-OSMOSIS PROPERTIES OF COLLAGEN FILMS CAST ON SOLVENT-FILLED METRICEL[a] FILTERS

Film No.	Collagen[b] Cast Wet Thick., mils	Collagen[b] Dried Film Thick., μ	Metricel[a] Filter Pore Size, Å	Oper. hours	Actual Flux, gfd	Calc. Flux[c] (2500 Å thick) Dry	Calc. Flux[c] (2500 Å thick) Wet	Salt Ret.,[d] %
18	20	2.44	4500	0.2	19.0 - -	187 -	238 -	16.9 - -
				0.69	19.4 - -	191 -	242 -	17.2 - -
73 A,B	50	6.10	2000	0.50	9.34, 9.65 -	228, 236	290, 299	27.7, 24.8 -
				0.95	9.60, 9.80 -	234, 238	297, 302	24.7, 22.5 -
				1.30	9.73, 10.0 -	237, 244	301, 308	28.5, 26.2 -
				3.10	9.33, 9.7 -	228, 236	290, 299	25.4, 23.9 -
73 D	30	3.65	75	3.10	0.274 - -	4.0 -	5.09 -	79.4 - -
89 B	none	none	75[e]	2.0	3.9 - -	- -	- -	23.2, 13.4 -
				3.0	4.2, 9.2 -	- -	- -	19.8, 12.8 -
89 C	none	none	75[f]	2.0	96.0, 18.0, 0.8	- -	- -	13.4, 16.2, 38.2

[a] Gelman Instrument Company, Ann Arbor, Michigan, cellulose triacetate filters.

[b] The collagen dispersion contained 0.64% collagen + 0.056% hexamethoxymethylmelamine in a 1:1 (wt/wt) mixture of water-methanol. This dispersion was cast on 1:1 water-methanol-wet Metricel filters, air-dried and crosslinked at 150°C for 6 hours.

[c] The calculated flux at 2500 Å thickness is based on both the wet and dry thickness, respectively, of the deposited collagen film (swelling ratio 1.27/1).

[d] Reverse-osmosis test conditions of 800 psi - 1.0% sodium chloride feed solution.

[e] Metricel PEM filter not heat-treated.

[f] Metricel PEM filter heat-treated at 150°C for 6 hours.

cast on porous, solvent-filled Metricel filters of 2000 Å and 75 Å average pore sizes followed by heat treatment at 150°C for 6 hours. Collagen films (73 A,B) of 6.1-μ dry thickness deposited on Metricel filters of 2000 Å average pore size gave salt retentions of 22.5 to 28.5% with calculated fluxes of 235 and 298 gfd. A 3.65-μ collagen film (73 D) deposited on the iridescent side of a Metricel PEM filter to 75 Å average pore size gave calculated fluxes of 4.0 to 5.1 gfd with 79% desalination.

To determine if the fine pore size of the PEM Metricel filter contributed to the desalinating ability of the deposited collagen film, a run (89 B) was made on 3 circles of unheated Metricel PEM filters alone with the iridescent side up. One of the 3 leaked and was shut down, while the other 2 films gave salt retentions from 12.8 to 23.2% with actual fluxes of 3.9 to 9.2 gfd. It was learned subsequently that heating the PEM Metricel to 121°C reduced the flux by 50%. Heating to 150°C with deposited collagen probably reduced the flux even more. Therefore, 4 circles of Metricel PEM filters which were heated to 150°C for 6 hours were tested under the same conditions and again gave varied results shown in run 89 C. The maximum salt retention achieved (38.2% at 0.80 gfd) was somewhat greater than that of the unheated filters (23.2%). Thus the low flux exhibited by film 73 D could be caused by the tightness of the heat-treated PEM Metricel. The 38.2% maximum desalination with the heated PEM Metricel indicates a substantial contribution toward desalination by the support.

The collagen films deposited on Metricel filters with pore sizes greater than 75 Å exhibited desalinations for brackish water somewhat less (26% compared with 47%) than that of the thicker collagen films evaluated as free films. Calculated product water fluxes (for a 2500 Å thickness) were about 6 times greater for the deposited films. This indicates imperfections in the deposited collagen films.

MECHANICAL PROPERTIES

The tensile properties of wet and dry collagen films were measured to determine the brittleness of the dried films and the effect of water plasticization on their mechanical properties.

For these tests, the collagen films were cast from a 0.78% dispersion of microcrystalline collagen in a 1:1 (wt/wt) solution of water-methanol. The film for dry-strength testing was cast 100 mils thick on wax-extended polyethylene sheeting taped to glass. After drying overnight at 47°C, it was removed from the surface and heat-treated at 150°C for 4 hours. The film for wet-strength testing was prepared in a similar manner except that the dispersion was cast 150 mils wet-thickness before drying and heat-treating. The latter film (0.89 mils dry thickness) was wetted with deionized water (2.1 mils wet thickness) and cut into 0.50 in. wide strips of 23 cm minimum length and the tensile properties determined in water at a crosshead speed of 0.2 in. per min. The thinner film (0.59 mils dry thickness) was

cut into strips in the wet state and then redried on flat, wax-extended polyethylene sheeting before testing. The results of the tensile tests are presented in Table 13 along with those for cellulose acetate films (determined previously) for comparison purposes.

The collagen films are highly plasticized by water which decreases their tensile properties greatly. The stiffness of the dry collagen film is decreased from a value of 29.8×10^3 kg/cm^2 for the dry film to only 0.049×10^3 kg/cm^2 for the wet film. The tensile strength is also greatly decreased (643 kg/cm^2 to 19.2 kg/cm^2). The elongation at break is increased from 3.9% to 28% and no yield point was evident from the stress-strain curve. Although the tensile properties of the wet collagen films are poor compared to the properties of the wet cellulose acetate film, the collagen films themselves held up well mechanically to reverse-osmosis tests up to 1500 psi pressure. The dry collagen film indicated good mechanical properties except for a somewhat low elongation at break, indicating a somewhat brittle nature. Observations from handling the dry collagen film indicated a poor tear strength which may probably be attributed to the highly crystalling nature of microcrystalline collagen and the films prepared from it.

DESALINATION OF MAGNESIUM SULFATE FEED SOLUTION

Because of their demonstrated high water transport properties, it was of interest to evaluate collagen films for brackish water desalination. The larger divalent cations and anions present in brackish water should be rejected to a greater extent than sodium chloride. Magnesium sulfate feed solution was chosen, therefore, to represent the divalent ions present in brackish water. A collagen film crosslinked by heat alone was chosen rather than the film crosslinked chemically with hexamethoxymethylmelamine since the latter films have much lower flux.

The film was prepared from a 0.64% dispersion in the manner used for the dry tensile specimens except that it was heat-treated at 150°C for 6 hours rather than 4 hours. The film was water-wet and mounted on wet No. 50 Whatman filter paper and tested at 800 psi pressure using 1% magnesium sulfate feed solution. The average data for the 3 circles are presented in Table 14.

The film held up well for 5.2 hours with actual fluxes of 5.0 to 5.2 gfd and 74.4 to 75.4% magnesium sulfate rejection. A limited life study was continued by allowing the film to stand in contact with the feed solution for 24 hours after the initial shut-down. It was restarted, run for an additional 1.6 hours, and shut down for 72 hours and then restarted again. Over this period, the actual flux increased slightly to 5.8 gfd and the magnesium sulfate retention fell to 69.3%, indicating a slight deterioration of reverse-osmosis properties. When the magnesium sulfate feed solution was flushed out of the unit and replaced with 1% sodium chloride feed solution and restarted, the flux increased to 6.87 gfd with 32.7% sodium chloride rejection.

TABLE 13

TENSILE PROPERTIES OF COLLAGEN FILMS

Film No.	State	Elastic Modulus, kg/cm^2 ($\times 10^{-3}$)	Yield		Break	
			kg/cm^2	Elong., %	kg/cm^2	Elong., %
2	Dry	26.0	500	2.9	568	3.3
5	↓	29.2	639	3.6	690	5.1
7	↓	34.2	635	2.6	670	3.1
Average	↓	29.8	608	3.0	643	3.8
3	Wet	0.052	-	-	21.0	28.5
4	↓	0.046	-	-	17.3	27.4
Average	↓	0.049	-	-	19.2	28.0
CA (Ave)[a]	Wet	17.4	207	1.75	207	16.9

[a] Tensile values for cellulose acetate film run wet and also reported in Table 5.

TABLE 14

REVERSE-OSMOSIS[a] PROPERTIES OF COLLAGEN FILM[b]
WITH MAGNESIUM SULFATE[c] FEED SOLUTION

Total Oper. Hours	Flux			$MgSO_4$ Rej., %
	Actual gfd	Calc. gfd (2500 Å thick)		
		Dry	Wet[d]	
0.5	5.2	235	757	74.8
1.5	5.2	239	769	74.9
2.7	5.2	237	763	75.4
4.2	5.0	228	734	74.6
5.2	5.1	234	753	74.4
	Shut down for 24 hours.			
6.8	5.5	252	812	72.3
	Shut down for 72 hours.			
7.52	5.8	265	822	69.3
	Shut down for 72 hours - flushed with deionized H_2O - charged with 1% NaCl feed solution and restarted.			
0.5	6.87	314	1010	32.7

[a] Values given are the average of 3 circles run.

[b] 100% collagen film; heat-treated at 150°C.

[c] 1% $MgSO_4$ feed solution at 800 psi.

[d] Wet thickness:dry thickness - 1.45 mils:0.45 mils (swelling ratio 3.22:1).

The desalination of sodium chloride feed solution of the same concentration was thus only one-half of that for the magnesium sulfate feed solution and about that expected for sodium chloride rejection by the collagen film.

Little if any detrimental lyotropic effect of magnesium ion on collagen would be expected since the sulfate ion has an inhibiting effect on the breaking of the secondary valence forces of collagen by the complexing action of the magnesium ion.[17] The lyotropic effects of cations in the presence of chloride ions would be expected to be much more pronounced and more detrimental to the life of the film.[17] Life studies of collagen films for brackish water desalination should therefore include the magnesium and calcium chlorides which exhibit the greatest lyotropic effect. The use of chemically cross-linked collagen film (hexamethoxymethylmelamine crosslinking agent) may reduce these lyotropic effects but at the expense of greatly reduced flux. The test does demonstrate that increased desalination could be expected with brackish water over that obtained for sodium chloride feed solution and that the theoretical flux rates for 2500 Å films would be high. It does not appear possible to realize the high flux potential by making asymmetric membranes by water gelation; gelation before crosslinking results in a slow redispersion of the film. Thus, techniques to prepare ultrathin membranes would be required to achieve the high flux potential of collagen.

ETHYL CELLULOSE

Ethyl cellulose has excellent salt rejection capabilities and it is noted for its strength, toughness, flexibility and resistance to alkaline hydrolysis. Its lack of high water permeability and its failure to yield satisfactory ultrathin films[18] have prevented the development of high flux films or membranes from ethyl cellulose.

It was thought that blending of a compatible polymer with high water sorption properties with ethyl cellulose would increase the flux and hopefully still maintain the high salt retention properties of pure ethyl cellulose. The evaluation of poly(diacetone acrylamide) indicated that it is highly plasticized by water and in addition gives low salt permeation values ($D_2K \sim 2.6 \times 10^{-12}$ cm^2/sec). Therefore, blends of poly(diacetone acrylamide) and ethyl cellulose were evaluated.

POLYBLEND FILMS

Poly(diacetone acrylamide) (PDAA), 0.41 g (1.6 intrinsic viscosity in acetone at 25°C) was added to 56 g of a 5.6% Ethocel* solution in anhydrous ethanol. The resulting solution had a slight haze. A 10-mil wet film was cast from this solution, air dried and finally heated to 59°C in a blower oven to complete the drying. The film (0.35 mil thick) removed from the plate by immersion in water was clear, indicating satisfactory compatability. In a

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* Dow Standard Grade Ethyl Cellulose, 100 cps viscosity, 48.5% ethoxyl content.

reverse-osmosis test* over a 46-hour operating period, the film exhibited salt-retention values in the range from 98.3 to 99.5%. The flux of the film ranged from 0.009 to 0.0124 gfd which corresponds to a calculated flux of 0.24 to 0.33 gfd at a thickness of 2500 Å. The water permeability, D_1C_1, calculated from the above reverse-osmosis data (5.3×10^{-9} g/cm-sec) is about the same as that obtained from osmosis data[19] (3.9×10^{-9} g/cm-sec) for pure ethyl cellulose film. The effect of the 10% added PDAA would seem to have been nil.

Polyblend films incorporating more PDAA were therefore investigated. A casting solution comprising 3.0 g of ethyl cellulose,** 0.76 g of PDAA (20% based on the ethyl cellulose) and 57 g of anhydrous ethanol was prepared. The casting solution again had a slight haze. A 10-mil film was cast from this solution and was transferred to a blower oven to dry at 55°C. The dried film had a slight bluish color when still on the glass plate but it was clear after removal from the plate by immersion in water. A reverse-osmosis test of this film at 1500 psi using 3.5% sodium chloride solution gave a calculated flux of 1.13 gfd based on a 2500 Å thick film with 71.5% salt retention after 2 hours of operation, and 1.2 gfd flux (2500 Å thickness) and 45.8% retention after 18 hours. The incorporation of 20% PDAA into ethyl cellulose thus increased the flux of the resultant polyblend film by 3.6 to 5.0 times that obtained for the 10% PDAA film. The decrease in salt retention may have been caused by the slight incompatability of the film containing 20% PDAA as noted by the slight bluish color of the dried film. The increased flux, however, was still only about 10% of the flux of cellulose acetate films of the same thickness.

Because of the slight incompatability, the small increase in flux noted and the decrease in salt retention at the 20% PDAA level, no further work was conducted with these polymer blends. Instead, efforts were directed toward the evaluation of ethyl cellulose of lower ethoxyl content and higher water absorption properties to determine the feasibility of preparing high-flux membranes from ethyl cellulose alone.

ASYMMETRIC MEMBRANES

The excellent salt rejection and low water permeability properties of ethyl cellulose films of different ethoxyl content have been documented by osmosis experiments by Merten, et al.[19] The water and salt permeability values from this work are tabulated below.

Ethoxyl Content, %	D_1C_1, g/cm-sec	D_2K, cm^2/sec
48	3.9×10^{-9}	3×10^{-11}
45.3	1.3×10^{-8}	4.5×10^{-11}
45	1.8×10^{-8}	1×10^{-11}

* 3.5% sodium chloride at 1500 psi.
** Dow Standard Grade Ethyl Cellulose, 100 cps viscosity, 48.5% ethoxyl content.

It is evident that the water permeability values of ethyl cellulose are much lower than that for 39.8% acetyl content cellulose acetate (D_1C_1 = 2.6 x 10^{-7}) determined by the same method. It is also evident that the ethyl cellulose with lower ethoxyl content (45 to 45.3%) shows water permeabilities 3 to 4.6 times greater than the standard 48% ethoxyl grade. The generally low water permeability values are probably associated with the low water absorption properties of ethyl cellulose. The water absorption properties of ethyl cellulose increase with decreasing ethoxyl content within a certain range. For example, the standard grade of ethyl cellulose with a degree of substitution (ds) of 2.5 absorbs ~ 2.5% water whereas ethyl cellulose of ds 2.2 (44.7% ethoxyl) absorbs about 4.0% water.* Ethyl cellulose with a ds of 2.0 would be expected to have an even greater water absorption and would be more desirable for membrane fabrication. The lowest ds material which is commercially available, however, is the 44.7% ethoxyl grade (ds 2.2)** with a viscosity of 51 cps. The 44.7% ethoxyl content ethyl cellulose was chosen, therefore, for a brief investigation of the flux characteristics of this material in the form of asymmetric membranes.

In the development of any new polymer in the form of an asymmetric membrane, it is necessary to progress according to established procedures. The first step includes a study of the solubility characteristics of the polymer and the selection of a suitable solvent or a mixture of solvents. The selection of a compatible non-solvent is followed by the addition of swelling agents which are compatible with all of the ingredients in the casting solution mixture. The parameters of membrane preparation which include casting and drying temperature, drying time and temperature, gelation temperature, heat-treatment, etc., must be correlated with modifications in the casting solution formulations to obtain the membrane with the optimum osmotic and physical properties.

Formulation Studies

Because of the lower ds of the 44.7% ethyl cellulose, its solubility, in comparison to that of the standard 2.5 ds ethyl cellulose, was found to be lower in most solvents and the range of solvents somewhat restricted. A mixture of ethyl acetate and ethanol gave a reasonable degree of solubility, but methyl acetate-methanol (4:1 ratio) and tetrahydrofuran were found to be the best solvents, giving quite viscous casting solutions with about 12% ethyl cellulose.

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* Ethyl Cellulose Product Bulletin, Cellulose Products Department, Hercules Powder Company.

** G-50 Ethyl Cellulose of Hercules Powder Company, Cellulose Products Department, Wilmington, Delaware.

Compatibility studies of several swelling agents were conducted with solutions of 2.2 ds ethyl cellulose in 4:1 methyl acetate:methanol solvent mixtures. Tartaric acid, maleic acid and zinc chloride were found to be incompatible with the polymer solution. Formamide and 70% perchloric acid were compatible and were used as additives to the casting solution formulations to increase the flux of the prepared membranes.

Ethyl cellulose (ds 2.2) casting solution formulations based on methyl acetate-methanol and also on tetrahydrofuran solvents were investigated. The following casting solutions based on methyl acetate-methanol mixed solvent with varying amounts of 70% perchloric acid were found to give membranes of adequate strength and flexibility when cast at room temperature and gelled in 0°C water after 2 to 3 min drying at room temperature.

Ethyl Cellulose (G-50)	10 g
Methyl Acetate (99+%)	48
Methanol	12
Formamide	15
70% Perchloric Acid	1.4 to 3.0

Membranes with poorer physical properties were obtained when the same formulation was cast at -11°C and dried for varying times up to ten min.

The following casting solutions based on tetrahydrofuran were also prepared.

	No. 27	No. 32
Ethyl Cellulose (G-50)	10 g	10 g
Tetrahydrofuran	50	50
Formamide	7	15
70% Perchloric Acid	1	2

The formulations were not optimized with respect to the formamide and perchloric acid additives. However, these casting solutions are promising from the standpoint of the amount of ethyl cellulose incorporated (13 to 14.7%) and the moderate solution viscosity obtained. Initial membranes prepared from these formulations, however, were weak and probably require the addition of a non-solvent with reformulation and further optimization of the casting, gelation and heat-treating procedures.

Ethyl Cellulose Membrane Evaluation

The ethyl cellulose (ds 2.2) membranes prepared from casting solution formulations based on methyl acetate-methanol mixtures were evaluated for

reverse-osmosis properties at 1500 psi using 3.5% sodium chloride feed solution and are presented in Table 15. Membrane 24, prepared from a casting formulation containing no perchloric acid, gave very low fluxes and poor salt rejection. Apparently the formamide, which has proven to be a good swelling agent and cosolvent for cellulose acetate membranes, did not function as a swelling agent in this formulation with ethyl cellulose. Membrane 24 (dried for 6 min) which gave 5.6 gfd flux was apparently overdried and its active layer had become porous. The incorporation of 70% perchloric acid swelling agent in increased amounts in membranes 26 and 28 gave improved flux and much better salt retention. A value of 4.2 gfd with 92.9% retention was achieved with membrane 28 (dried for 3 min). The 3-min drying time was approximately the optimum for this formulation under these conditions. Increasing concentrations of perchloric acid (membranes 33 and 34) resulted in a flux of 4.25 with 93.3% retention with membrane 34 (dried for 2 min).

Membranes which were cast and dried at -11°C and those cast and dried for only 1 min at room temperature had poor physical properties. During gelation, they became opaque and badly buckled or wrinkled and became worse after heat-treatment.

The effect of perchloric acid addition on the osmotic properties of ethyl cellulose membranes is shown more clearly in Table 16. Although slightly better osmotic properties were obtained for ethyl cellulose membranes (membrane 34 dried for 2 min) prepared with 3.0 g of perchloric acid, the effect appears to level off at about 1.43 g of perchloric acid (membrane 28 dried for 3 min) which gave osmotic properties of 4.2 gfd with 92.9% salt retention. Optimization of the casting formulation with respect to ingredients other than perchloric acid with subsequent optimization of casting and gelation conditions would be expected to give improved results. For example, neither the effect of a greater percentage of water other than that introduced with the 70% perchloric acid nor variation in the amount of cosolvent formamide has been investigated. The initial results, however, encourage further work to take advantage of the expected durability of ethyl cellulose. An ethyl cellulose of even lower ds (about 2.0) would be particularly attractive for further work.

CONCLUSIONS AND RECOMMENDATIONS

Poly(vinylene carbonate) was shown in previous work to have excellent intrinsic osmotic properties, however, efforts to prepare high flux, high salt retention asymmetric membranes from this polymer have not been successful. Ultrathin films of the polymer exhibit excellent osmotic properties initially, but after a few hours the flux and salt permeation begin to rise. This phenomenon was traced to excessive brittleness of the polymer which leads to rupture of ultrathin films when pressurized against even the most minute irregularity in the support material. In efforts to overcome this difficulty, a study of vinylene carbonate copolymers was undertaken, but the only copolymers prepared still had unacceptable mechanical properties.

TABLE 15

MEMBRANES FROM ETHYL CELLULOSE (44.7% ETHOXYL CONTENT)

	Membrane Casting Conditions				3.5% NaCl Sol'n. - 1500 psi	
Membrane No.	Drying Time, min	Casting Temp., °C	H_2O Gel Temp., °C	3-min Heat Treat., °C	Prod. H_2O Flux,[a] gfd	Salt Rej.,[a] %
24	1	ambient	ambient	none	<3.0	57.4
	3	↓	↓	↓	none	-
	6				5.6	45.5
	3	-11	0	90	none	-
	6	↓	↓	↓	↓	-
26	1.0	ambient	ambient	none	27.2	54.5
	1.5	↓	↓	↓	14.8	68.8
	2.0				4.4	80.7
	3.0				5.0	81.4
28	1.0	ambient	ambient	80	7.5[b]	75.6[b]
	1.5	↓	↓	↓	6.3	82.2
	2.0				3.9	91.4
	3.0				4.2	92.9
	1.0	-11	0		15.0[c]	12.7[c]
	2.0	↓	↓	↓	3.5	82.8
33	1.0	ambient	0	80	Too porous	
	2.0	↓	↓	↓	3.8	89.2
	3.0				4.6	89.3
	1.0	-11			Membrane defects	
	3.0	↓	↓	↓	↓	
	10.0				Too porous	
34	1.0	ambient	0	80	Ruptured	
	2.0	↓	↓	↓	4.25[d]	93.3
	3.0				3.8	91.1
	1.0	-11			Membrane defects	
	3.0	↓	↓	↓	↓	
	10.0				Too porous	

Casting Solution Formulation, g for Membranes	24	26	28	33	34
Ethyl Cellulose, G-50	10	10	10	10	10
Methyl Acetate	53	44	48	48	48
Methanol	13	11	12	12	12
Formamide	10	15	15	15	15
70% Perchloric Acid	0	1	1.43	2	3

[a] Average values for 3 samples run.

[b] One sample only.

[c] Average values for 2 samples run.

[d] One circle tested had 94.5% rejection/4.25 gfd.

TABLE 16

EFFECT OF 70% PERCHLORIC ACID SWELLING AGENT ON ETHYL CELLULOSE[a] MEMBRANES

Amt. of 70% $HClO_4$ in Casting Formulation (g/10 g Ethyl Cellulose)[c]	Membrane No. and Drying Time (min)	3.5% NaCl Sol'n. - 1500 psi	
		Flux,[b] gfd	Rejection,[b] %
0.0	24-1	<3.0	57.4
1.0	26-3	5.0	81.4
1.43	28-3	4.2	92.9
2.0	33-4	4.6	89.3
3.0	34-2	4.25[d]	93.3[d]

[a] Ethyl cellulose of 44.7% ethoxyl content.

[b] Average values for 3 circles tested.

[c] See Table 15 for complete formulation.

[d] Best single circle gave 94.5% rejection with 4.25 gfd flux.

External polymeric plasticizers also failed to improve the physical properties, while at the same time maintaining the excellent osmotic properties of poly-(vinylene carbonate).

The outstanding chemical stability and excellent strength available with nitrile polymers suggested their applicability to membrane fabrication. Early work showed that polyacrylonitrile had a salt retention limited to 30 or 40%, although membranes of high flux could be prepared from it. It too exhibited excessive brittleness and therefore polymethacrylonitrile was investigated in an effort to prepare a more flexible nitrile membrane. Although polymethacrylonitrile had satisfactory mechanical properties, its osmotic properties were no better than those of polyacrylonitrile. Neither partial hydrolysis nor the incorporation of comonomers was effective in significant increases in salt retention. Although it is doubtful that high retention membranes can be obtained from nitrile polymers, they might find use in waste water recovery where their excellent chemical stability and biological resistance will prove to be of value.

Films prepared from microcrystalline collagen proved to have very high intrinsic water permeability and retained in excess of 75% of magnesium sulfate. It thus appears that sufficiently thin membranes of collagen could find use in brackish water desalination. Further progress with this material will require the development of a method to prepare supported ultrathin films.

Promising osmotic properties have been obtained with asymmetric membranes prepared from ethyl cellulose of low degree of substitution. It is believed that high retention, high flux membranes which retain the good mechanical properties and stability to alkaline hydrolysis of the commercial ethyl cellulose polymers can be made from an ethyl cellulose having a degree of substitution lower than that now commercially available. The very promising properties of ethyl cellulose recommend it for further study including the synthesis and evaluation of polymers of low (2.0) degree of substitution.

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